THERMODYNAMICS OF
LIQUID COPPER SILVER ALLOYS

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of

MASTER OF TECHNOLOGY

BY

UPPAL VEERAIAH CHOUDARY

DEPARTMENT OF METALLURGICAL ENGINEERING

Indian Institute of Technology Kanpur

AUGUST 1969

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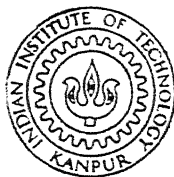
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by

UPPALA VEERAIAH CHOUDARY

to the

Department of Metallurgical Engineering
Indian Institute of Technology, Kanpur

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CERTIFICATE

Certified that this work on "Thermodynamics of liquid Copper – Silver alloys" has been carried out under my supervision and that it has not been submitted elsewhere for a degree.

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ACKNOWLEDGEMENTS

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LIST OF SYMBOLS

A, B — Metals

C, D — Empirical constants

a_i — Activity of ith component

e_M^o — Interaction coefficient of oxygen with metal M in the melt

E — Electromotive force, mV

f^o — Activity coefficient

F — Faraday constant, kcal/mV equivalent

F_i^M — Relative partial molar free energy of mixing, of ith component, cal/g-atom

H_i^M — Relative partial molar enthalpy of mixing of ith component, cal/g-atom

S_i^M — Relative partial molar entropy of mixing of ith component, cal/^{o}K g-atom

F^M, H^M, S^M — Integral molar properties of mixing

F^E, S^E — Excess molar properties of mixing

K — Equilibrium constant, atm^{-1}

P_{o2} — Partial pressure of oxygen, atm

R — Universal gas constant, cal/^{o}K mole

T — Temperature, ^{o}K

x_i — Mole fraction of ith component

α_{Cu} — Alpha function for copper

β_{Cu} — Beta function for copper

γ_i — Activity coefficient of ith component

ΔF_{fusion} — Free energy of fusion of copper, cal/g-atom

ΔS_{fusion} — Entropy of fusion of copper at 1356°K, cal/^{o}K g-atom

SYNOPSIS

THERMODYNAMICS
OF
LIQUID COPPER - SILVER ALLOYS

U.V. CHOUDARY

The reversible galvanic cell:

$$Cu \ (S), \ Cu_2O \ (S) \ // \ CaO - ZrO_2 \ // \ Cu - Ag \ (1), \ Cu_2O \ (S)$$
electrolyte
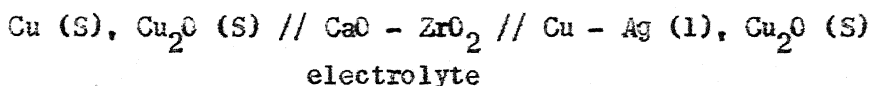
was employed to determine the thermodynamic properties of the liquid copper-silver alloys in the range of X_{Cu} from 0.1 to 0.8 and temperature from liquidus to $1330^{o}K$. The liquidus temperatures of silver-rich alloys determined from the few measurements did not match with the phase diagram values. The activities of copper were found to be higher than the values reported by Hultgren et al in the silver-rich side, whereas they agree well in the high copper side, F^M and F^E values obtained by extrapolation of data in this study agree well with those reported in literature. H^M values of this study agree with the calorimetric results within the experimental uncertainity. Small values of S^E of this work, confirm the nearly regular behaviour of Cu - Ag system.

INTRODUCTION

A knowledge of thermodynamic properties of metallic solutions is extremely useful for the understanding of various metallurgical processes. For instance, thermodynamic data are needed to formulate the conditions of equilibrium between the alloys and a gas phase or slag. Also, thermodynamic data give a quantitative basis for better understanding of the peculiarities of phase diagroms and constitution of various metallic phases. Solutions of interest to the metallurgist can be binary, ternary or more complex containing number of components. To understand the nature of complex solutions, basic thermodynamic data of binary solutions will be of great help. At present data are available for barely 200 binary systems out of the 3000 and odd possible systems. Even amongst these well studied systems, the thermodynamic properties an some times known with less precision and more accurate data are needed.

Thermodynamic investigations usually consist of experimental determination of either the integral molar enthalpy of mixing or heat capacities by calorimetric methods or the partial molar free energies utilizing the various equilibrium measurements, such as electromotive force, vapor pressure, chemical reaction equilibria and distribution equilibria. Equilibrium methods afford the direct determination of free energies of mixing and the

activity values in some systems $\underset{\text{are}}{\angle}$. known with less than 2% uncertainity.

Electromotive force methods and vapor pressure measurements are more popular among the equilibrium methods, and more than 75% of the binary systems were studied by these methods. For activity determinations the equilibrium methods an considered more reliable than the calorimetric methods.

Literature survey revealed that the thermodynamic properties of Cu-Ag system are in error. Hence it was decided to investigate the thermodynamics of Cu-Ag system by electromotive force (emf) method using solid electrolyte. This technique has already been established as one which is capable of yielding accurate results.

CHAPTER II

LITERATURE SURVEY

II. 1. Considerations of solid electrolyte galvanic cells.

A. Introduction:

Solid electrolytes can be considered as solid inorganic compounds or phases with well defined cryst-alline structure and exhibiting ionic conduction in a considerable ranges of temperature and chemical potentials of metal or non-metal conducting species. Though various solid electrolytes such as halides and oxides were used right from the beginning of this century, keen interest was evinced in solid electrolyte galvanic cells only after the classic work of Kiukkola & Wagner (42) in this field. A host of papers published in the last ten years, bringing forth the various applications of solid electrolytes, stand testimony to the versatality of these. Mostly solid oxide electrolytes have been used in a variety of metallurgical investigations undertaken in the recent years and hence complete attention will be devoted to the oxide solid electrolytes.

B. Solid oxides as electrolytes:

The total electrical conductivity of the solid electrolytes may be expressed as the sum of three terms

where σ_{ion}, $\sigma_{\oplus}$ and $\sigma_{\ominus}$ refer to the conductivities of ions, electron holes and electrons in the electrolyte.

Electrical conductivity of these oxides vary as a function of temperature and partial pressure of oxygen (Po_2) prevailing over the oxides. Below a critical partial pressure, conductivity due to electrons becomes significant whereas above an upper limit of p_{O2}, electron hole conduction predominates. In the intermediate range of oxygen partial pressures, conductivity is constant with temperature and is primarily due to the ions alone. If an oxide has to be used as electrolyte in a solid electrolyte galvanic cell, its conductivity should be almost wholly due to oxygen ions, i.e., transport number of oxygen ions t_o^{2-} should be close to unity, in the temperature and partial pressure ranges of interest. Simple binary oxides with few exceptions like BeO(73) and SiO_2 (44)are found to be unsuitable because of their considerable electronic conduction. Some of the oxides eg: Al_2O_3 (44,71,144), MgO (44,59,144) and rare earth oxides (44,74,111) exhibit complete ionic conduction only in a very narrow ranges of temperature and p_{O2}. Hence they are of little interest in many applications involving solid electrolytes.

For extending the ranges of temperature and p_{O2} in which t_{O2-} is almost unity, doping of the simple binary oxides with aliovalent oxides have been found to be of immense help. Especially the solid solutions of tetravalent oxides ZrO_2, ThO_2 or HfO_2 with lower valent oxides CaO, Ya_2O_3, Y_2O_3 or MgO have received increasing

attention over the years. These have fluorite (CaF_2) type structure with oxygen ion defects resulting from the substitution of lower valency cations Ca^{++}, Mg^{++}, La^{3+}, or Y^{3+} for the tetravalent Zr^{4+}, Th^{4+} or Hf^{4+}. Hund (56) and D. Roy & R. Roy (67) reviewed the various types of solid solutions formed when a fluorite type solvent is doped with aliovalent cations. Extensive conductivity measurements on these solid solutions, under varied conditions of p_{O2} and temperature, helped in the diagnosis of electronic conduction limits and establishment of the 'ionic plateau'. Out of various solid solutions with fluorite structure, calcia-stabilized zirconia and yttria stabilized thoria have been more popular due to their exclusive ionic conduction in a wide spectrum of oxygen partial pressure. Various studies (42,43,47,48,66,74,76, 137 e, 138,144,145,148) employing doped zirconia and doped thoria have clearly established the temperature and p_{O2} limits for ionic conduction ($t_{O_2-} > 0.99$).

C. <u>Principle of electromotive force (emf) methods using solid oxide electrolyte galvanic cells</u>:

From the first and second laws of thermodynamics, free energy change for a reversible process is given by

$$dF = VdP - SdT - \delta w' \qquad (1)$$

dF is the Gibbs free energy change; V, P, S, T have usual significance; and w' is the work done by the system other than that against pressure. At constant temperature and pressure above Eq. reduces to $dF = -\delta w'$ (2)

on intergration, we have $\triangle F = -W'$ (3)

In the galvanic cell the work to be considered is the electrical work done when transport of charge takes place from one potential to another. Consider the following galvanic cell:

$$\text{Electrode} \,\underset{\mu_{O_2} I}{//} \quad \text{Solid oxide electrolyte} // \,\underset{\mu_{O_2}^{II}}{^+\text{Electrode II}}$$
$$(t_{O2} \simeq 1)$$
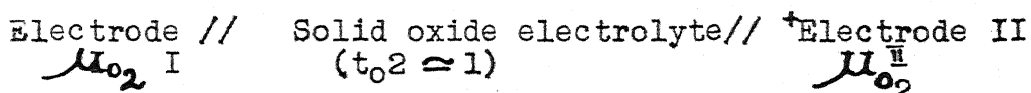
The emf of above galvanic cell results from the difference in chemical potentials of oxygen $\mu^I_{O_2}$ & $\mu^{II}_{O_2}$ at the left and right electrodes. Assuming that the oxygen ions are the chief conducting species in the electrolyte, the emf of the above galvanic cell can be related to the free energy change of the cell reaction $O_2(II) = O_2(I)$ (4)
If the emf of the cell is E volts and the reaction taking place is accompanied by passage of n Earadays is nF cuolombs, the work done by the system in the cell is nFE volt cuolombs. Therefore, according to the eq.(3)

$$\Delta F = \mu^I_{O_2} - \mu^{II}_{O_2} = - nFE \tag{5}$$

Since the reaction(4) takes place by passage of 4 faradays, n=4. If $\mu_o{}^0{}_2$ and $p_o{}^0{}_2$ represent the chemical potential and partial pressure of oxygen, Eq. (5) can be written as

$$\left(\mu_{O_2}{}^0 + RT \ln \frac{p_{O_2}{}^I}{p^0{}_{O_2}}\right) - \left(\mu_{O_2}{}^0 + RT \ln \frac{p_{O_2}{}^{II}}{p_{O_2}{}^0}\right) = -4FE \tag{6}$$

where $p_{O_2}{}^I$ & $p_{O_2}{}^{II}$ are equilibrium oxygen partial pressures at left and right side electrodes; R is gas constant; T is the absolute temperature.

Simplifying Eq.(6)

$$E = \frac{RT}{4F} \ln \frac{p_{O_2}{}^{II}}{p_{O_2}{}^I} \tag{7}$$

usual convention of cell emf is adopted - the cell emf
is taken as positive when positive current flows through
external circuit from right to left. If oxygen potential
or p_{O_2} is known at one electrode, oxygen potential at the
other electrode can be calculated from the cell emf, using
eq.(7)

D. General features of solid oxide electrolyte galvanic cells:

A galvanic cell assembly consists of an electrolyte
with appropriate electrodes in close contact with the ele-
ctrolyte Lead wires in contact with the electrodes act as
pure electronic conductors and emf developed as a result
of cell reaction can be measured by a convenient potential
measuring device. To measure meaningful emf , various
features of the galvanic cell have to be analyzed. Main
considerations in the setting up of galvanic cell are
discussed below.

D.1 Solid electrolytes:

Solid electrolytes can be used successfully in
various applications, provided they satisfy certain prere-
quisites.

(i) They should have high thermodynamic stability
at high temperatures. These should not undergo any trans-
formation in the experimental temperature range.

(ii)   For certain applications such as oxygen determination in steel making, the solid electrolyte should possess high thermal shock resistance. Either by altering the composition of the stabilizing agent or using altogether different electrolytes, desired thermal shock resistance have been achieved without making much compromise to the ionic behaviour of the electrolyte. Diaz and Richardson (143) have reported that 7 mol% lime stabilized zirconia has superior thermal shock resistance than the more popular 15 mol% composition, at the same time exhibiting satisfactory ionic conduction.

(iii) Solid electrolytes should be impervious to gases and should have as high a density as possible. Single crystal specimens of electrolyte are well suited because of their high purity, high density and low surface area. Many of the solid electrolytes in use are difficult to get in single crystal form. Pressed and sintered pellets, crucibles or tube shapes served the purpose. High density and impermeability to gases is achieved by employing maximum possible sintering temperature, as high as $2200^{o}C$.

(iv)   Solid electrolytes should exhibit predominant oxygen ion conduction and neghigible electronic conduction under experimental conditions of temperature and partial pressures. For conditions of complete ionic conduction ($t_{o2} > 0.99$), the simple relation between the

emf of the cell and the free energy of the reaction,

F = - nFE is valid. But if electronic conductivity is
appreciable (T_e 0.01) ,knowledge of t_{o2-} as a function
of chemical potential of oxygen is essential to relate the
cell emf and the free energy change. Under these condit-
ions, it can be shown that (52)

$$ E = \frac{1}{4F} \int_{\mu_{O_2}^{I}}^{\mu_{O_2}^{II}} t_{O^{2-}} \, d\mu_{O_2} \qquad (8) $$

An accurate evaluation of the above integral is
rendered difficult due to the lack of precise knowledge
of variation of t_{o2-} with oxygen potential (μ_{O2}). However,
if an electrolyte with mixed conduction has to be used for
a particular application, two approaches can be followed
for evaluating the above integral. Analytical approach
to the above problem has been suggested by Schmalzried(44).
By the introduction of two parameters $P_\oplus$ and $P_\ominus$ which
are defined as the oxygen partial pressures at which σ_{o2-}
equals $\sigma_\oplus$ and $\sigma_\ominus$ respectively, he derived $t_{o2} - p_{o2}$ relation-
ships for various types of electrolyte systems. Second
approach is due to Rapp (74), which is essentially a
graphical integration of the above equation from the plot
of t_{ion} vs chemical potential of oxygen.

An analysis of the problems arising from electronic
conduction and theoritical derivation of cell emf under
conditions of mixed conduction can be found in the papers
by Steele (102), Schmalizried (44), Pal'guev. ' (43) and

Rapp (74). Aforementioned approaches are valid only if internal 'short circuiting' behaviour of electronic conductivity is not detrimental to stability of the cell emf with time. When the electronic conductivity is considerable, oxygen is continuously transferred from higher oxygen potential electrode to lower oxygen potential electrode. Unless the relevant electrochemical reactions and mass transport processes are rapid, the flux of oxygen may distrub the oxygen potential at the electrodes resulting in either lower cell emf or continuous decrease in cell emf till it drops down to zero (102).

(v) Solid electrolytes should be chemically unreactive to the electrodes employed and the cell reaction at the electrode- electrolyte interface should be unambiguous and clearly defined. The local thermodynamic equilibrium at the interface is affected if there is dissolution of electrode components or chemical compound formation as a result of chemical reaction between the electrolyte and electrode. These may bring about change in relative concentrations of electrode constituents or affect the Kinetics of relevant electrochemical reactions and hence produce erroneous emf values. Normal reversibility tests employed to test the performance of the cell will be useful in detecting the deviations of the cell from reversible behaviour.

No single electrolyte may satisfy all the above requirements. Therefore one has to choose the electrolyte with care.

D.2 Electrodes:

Electrodes can be solid, liquid or gaseous. One of the electrodes in the galvanic cell is of known oxygen potential and is usually termed as the reference electrode. The electrodes should be quite reversible and have as much 'oxygen buffer capacity' as possible to guard them against possible polarization effects and minor side reactions. Among solid electrodes, Fe- FeO mixture is shown to be highly reversible(102). Usual preparation of solid electrodes consist of thoroughly mixing the electrode mixture pressing them into compacts and sintering them at the desired temperature. Since electrode mixture contains either two or more phases (metal-metal oxide or two oxide mixtures), powders employed should be as fine as possible to allow rapid equilibration in the electrolyte. If either crucible or short tube electrolytes are used, the finely ground electrode mixture can be sintered 'insitu inside the electrolyte. The lead wires commonly employed are platinum wires welded to a platinum disks well pressed against the two electrodes. If different lead wires are used, the thermoelectric potential of the two leads must be determined and necessary corrections should be made to the cell emf.

Liquid electrodes consist of either liquid metal in equilibrium with its oxide (134) or liquid metal with a known amount of oxygen dissolved in it (141,143). As a rule, liquid electrodes perform better than solid electrodes provided there are no corrosive effects on the electrolyte employed. Electrolyte used is in the form of crucible or tube which serves as container for one of the electrodes. The leads used should dissolve as little as possible in the electrodes. Leads can be either be dipped momentarily during the time of emf measurement or continuously immersed if the solubility of the lead in the electrode is neghigible. For instant dipping Ta (141), Mo (142), Pt (12,137), stainless steel (143), Ir (134), Ni-coated with NiO (116) and many others were used whereas for constant immersion, sintered oxides such as Cr_2O_3 (142) and cermets (137,143) were preferred. Continuous dipping of lead is recommended though instant dipping leads will give accurate emf in the absence of dissolution reaction accompanied by spurious emf. For solid electrolyte applications above $1600^{o}C$, liquid metal with oxygen dissolved, low enough not to form an oxide, is highly suitable to avoid the corrosive effects of oxide on the solid electrolyte (52,P 56).

Gaseous electrodes consist of gas mixtures of either known or unknown oxygen potential, flowing over supporting electrode such as Pt in close contact with electrolyte tube (55, 128, 138, 143,148). These electrodes are convenient, provided there is no leakage between the two electrodes of the galvanic cell. These are often better than solid electrodes where various interface deteriorations may develop during operation of the cell.

D.3 Cell assembly:

Various designs of cell assembly are possible and the choice of particular design is dictated by the system being investigated. The earliest investigations using solid electrolyte galvanic cell for determination of free energies of formation of oxides, were done by Kiukkola & Wagner (42). They employed "open cell stacked pellet-technique" wherein the solid electrodes were kept firmly pressed to either side of the electrolyte and the cell was operated under a flow of inert gas. This kind of simple cell assembly has been found to be adequate for high oxygen potential systems but proved to be unreliable for investigations involving low oxygen potential systems. Also a gas transport from one electrode to another is a serious problem in this simple cell assembly, possibly resulting in mixed potentials. Various improvements have been affected in the latter cell designs by

Carter (110); Schmalzried (81,111); Goto & Matsushita(46); Steele & Alcock (47) and Charette & Flengas (108). In all these designs, attempts have been made to promote local thermodynamic equilibrium by keeping loose electrode mixture around the electrodes and also by providing individual compartments for the electrodes with seperate inert gas streams. Steele & Alcock (47) tried to achieve this by pressing two polished alumina tubes to the electrolyte surface on each side with seperate gas stream in each tube. Intermixing of gas streams of the two electrodes cannot be completely ruled out in this kind of design. Charette & Flengas (1^8) used hermetically sealed half cell compartments with large amounts of electrode mixtures and operated the cell in vaccum. This improved design gave rapid cell response and stable emf's could be recorded over periods of even several weeks. For liquid systems, solid electrolyte crucibles can be employed if the particular geometry does not affect the cell emf by way of gas transport. Galvanic cell assemblies with crucible electrlytes were successfully used by various investigatiors (116,123,126,134). If one of the electrodes is gaseous or the gas transport problem is acute, one end closed electrolyte tubes with seperate gas streams can be employed. Many emf measurements (123,125,133,137, 139-144) have been made in molten metals and gas mixtures using the tubular geometry. Since the cost of the tube electrolytes is too prohobitive for routine applications

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(eg: oxygen monitoring in steels). A disk electrolyte sintered to one end of quartz tube has been developed (138,148). These are good for instantaneous oxygen determinations in molten metals and can be discarded whenever a failure in the electrolyte occurs. Electrolyte discs can be cemented to a supporting tube such as alumina. If the seal between the disk electrolyte and supporting tube is good it can be used for oxygen partial pressure measurements in gas mixtures. Such an oxygen gauge has been successfully devised by Weissbart & Ruka (128). Attention should be paid to the constancy of temperature across the cell assembly. This can be taken care of by using a furnace of considerable constant temperature zone or alternatively making the cell assembly as small as possible. In the presence of temperature gradient across the cell, thermal emf should be taken into account for precise interpretation of cell emf's. Also, the cell assembly should be surrounded by a grounded metal sheath so as to avoid the spurious emfs arising from furnace windings and ancillary control equipment.

D.4 Cell atmosphere:

In many applications, galvanic cell measurements are made either under vacuum or inert atmosphere. Purified He, Ar or N_2, devoid of either oxidizing or reducing impurities, can be used for this purpose. By successively passing the gas through one or more of the furnaces

with Cu turnings, Mg chips, Ti sponge or Zr-Ti alloys, traces of oxygen and hydrocarbons in the inert gas can be removed to quite an extent. Moisture and CO_2 can be eliminated with the help of $Ca\,Cl_2$, P_2O_5 and liquid oxygen traps. To prevent the accumulation of released impurites in the vicinity of the cell, dynamic vaccum or flowing stream of purified gas is preferred. While operating the cell under vaccum, special trap to prevent the back diffusion of pump vapors should be set up. Steele & Alcock (47) have obtained the same emf values under inert gas flow as well as vaccum, demonstrating that there are no special advantages in the use of vaccum. To minimize mixed potentials, independently purified gas streams after prior equilibration with the electrode mixture, should be admitted into seperate compartments of the galvanic cell.

D.5 Emf measuring devices:

Open circuit emf of the galvanic cell can be measured by a variety of devices-potentiometer, oscilloscope bridge*, valve voltmeter[102] or electrometer [102,143]. Potential measuring device should pass as little current as possible through the cell without causing undue polarizations at the electrodes. Care should be taken while measuring emf by oscilloscope bridge and electrometers as these are more susceptible to extrameous emf pickup. If the resistance of the electrolyte is not too high (usually

* Activities in molten alloys - EMF methods) - K. OKAJIMA & H. SAKAO J.JAP. INST. METALS, 9, 47, 1968.

above 800°C), potentiometer is preferred. For cells
with higher resistances, other devices like vibrating
read electrometer will be a better choice(102). Emf mea-
surements were reported to a temperature as low as 350°C ,
using the electrometer (103).

D.6 Reversibility criterion in galvanic cells:

Once the galvanic cell is in operation, rever-
sibility of the cell emf has to be demonstrated by distu-
rbing the local thermodynamic equilibrium. Reversible
behaviour of the cell can be established by the following
checks.

(i) A small amount of current, of the order of
microamperes is passed through the cell first in one dire-
ction and next in the opposite direction, for at least half
an hour. The cell becomes polarized and initially either
decrease or increase in cell emf is noticed depending on
the direction in which current is passed. The cell emf
is observed with time and the quick stabilization of emf
denotes good reversible behaviour of the cell. Solid
systems are more prone to polarization effects and hence
take considerably long time to reach equilibrium.

(ii) After equilibrating the cell at a parti-
cular temperature, the stability of emf with time should
be observed over a period of twelve hous. The constancy
of emf during this period, indicates possible reversibility
of the cell.

(iii) Reproducible emf should be observed
at the same temperature in both heating and cooling cycles
of the cell. At least one temperature excursion should
be done.

(iv) Flow rate of the gas stream can be
varied and its effect on cell emf should be studied. If
the emf is stable for a reasonable variations of flow
rate, it can be considered reversible provided preceding
checks also confirm this. Also small amounts of gaseous
impurities can be injected in the gas stream and the
quick return of emf to equilibrium indicates reversibility.

II.2   <u>APPLICATIONS OF SOLID ELECTROLYTE GALVANIC CELLS</u>

A.   <u>Introduction</u>

      Solid electrolyte galvanic cells have been useful in obtaining precise thermodynamic data for various metal oxides, solutions of metals or oxides. Also, accurate studies of number of new alloy systems and nonstoichiometric compounds have become possible. Continuous measurement of oxygen contents in liquid metals and in various gas mixtures has led to new control methods in various metallurgical industries. Various other applications include the determination of phase boundaries, diffusion coefficients of oxygen in solid and liquid metals and corrosion behaviour of materials. Numerous kinetic studies such as rate of deoxidation of steels, rates of oxidation and reduction of metals and metal oxides have been done in the recent years. Principles of most of these applications are outlined below.

B.   <u>Free energies of formation of simple and compound oxides -</u>
<u>Nonstoichiometric studies</u> :

B.1   <u>Simple oxides</u>

      Free energies of formation ($\triangle F^{0}$) of various metal oxides can be accurately determined from the reversible emf of the cells of the type

$$A, A O \; // \; \text{Solid oxide} \; // \; B, B O \; (\; O_2, \text{ air etc}) \quad \boxed{1}$$
$$\text{Electrolyte} \qquad\qquad \text{Reference electrode}$$
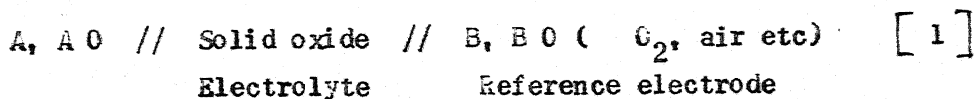
The emf can be thought to be either due to the displacement reaction

$$A + BO = B + AO \qquad (1)$$

or due to the oxygen potential difference on either side of the electrolyte

$$\frac{1}{2} O_2 (A, AO) = \frac{1}{2} O_2 (\text{Ref. electrode}) \qquad (2)$$

If the oxygen potential in the reference electrode is fixed either by controlled gas mixtures or with a metal and metal oxide of known free energy of formation (BO in cell), the free energy of formation of unknown metal oxide can be accurately determined from the reversible cell emf using the relation

$$\triangle F^O_{BO} = \triangle F^O_{AO} - n F E \qquad (3)$$

Various metal oxides (when A, B = Cu, Pb, Ni, Co, Sn, Ec, Mn, Mo, Cr, U, V, W, Nb) have been studied (42, 43, 46, 47, 88, 92, 95, 99, 100, 107) by this technique. Since the cell emf's can be measured to an accuracy better than 1 millivolt in many cases, the overall uncertainity in the free energies of formation can be reduced to 100 calories per mole of oxygen.

B.2. Compound oxides

Free energy of formation of a variety of compound oxides such as spinels (81, 84, 89, 93, 105), silicates (93), molybdites (105), tungstates (83) have been determined using the galvanic cell of the type

$$A, B_2O_3, AB_2O_4 \; // \; \text{Solid oxide} \; // \; A, AO \qquad [2]$$
$$\text{Electrolyte}$$
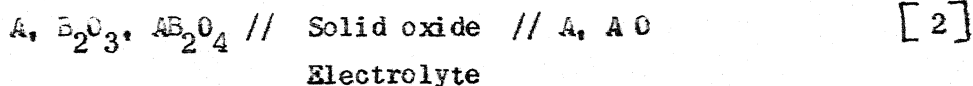
Overall reaction can be considered as

$$B_2O_3 + AO = AB_2O_4 \qquad (4)$$

$$\Delta F^o_{AB_2O_4} = -nFE \qquad (5)$$

Precautions have to be taken to ensure reversible electrode reaction in this kind of cells. The equilibration of oxide phase mixtures is sluggish and hence intimate mixture of the oxide phases has to be prepared by repeated grinding and sintering at suitable high temperatures. Since a stable cell emf requires a passage of small amounts of current to result in presumed equilibrium cell reaction, ionic reaction components in oxide phase mixtures should have high enough mobility to establish the necessary local thermodynamic equilibrium.

An interesting variation of the galvanic cell is used to measure the dissociation pressures of two phase mixed spinel-wustite composition $(A, B)_3O_4 - (A, B)O$ and the cell can be depicted as

$$A, AO \;//\; \text{Solid oxide} \;//\; (A, B)_3O_4, (A, B)O \qquad [3]$$
$$(p^o_{O_2}) \qquad\qquad \text{electrolyte} \qquad\qquad (p_{O_2})$$
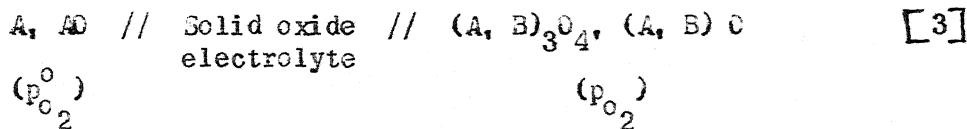
Such studies have been carried out on a number of spinel solid solutions of the type $(Fe, B)_3O_4$ where $B = Ni$, Mg, Mn, Co (86, 110, 115). The cell was set up with the prepared composition of $(Fe, B)_3O_4$ solid solution spinel phase on the right side and the current was passed to reduce the spinel. The cell reaction is the oxygen transport from right to left side of the electrolyte. If the reduction product were wustite of same Fe : B ratio, the cell emf would be invariant to further passage of moderate amounts of

current once the small initial current had been passed to establish the second phase. This was observed in the case of spinel solid solution range Fe_3O_4 to $Fe_{2.4}Co_{0.6}O_4$, by Carter (110).

Cell reaction at right: $\quad 2Fe_{3-x}B_xO_4 = 6B_{\frac{x}{3}}Fe_{1-\frac{x}{3}}O + O_2 \qquad (6)$

Cell reaction at left : $\quad 2Fe + O_2 = 2FeO \qquad\qquad\qquad (7)$
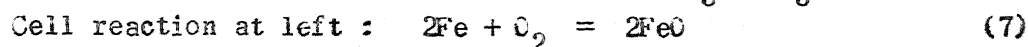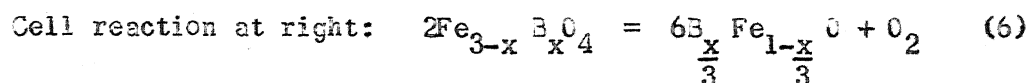
Dissociation pressures of spinel solid solution (p_{O_2}) is given by the relation

$$\ln p_{O_2} = \ln p^0_{O_2} - \frac{n\,FE}{RT} \qquad (8)$$

Free energy of formation of $(Fe, B)_3O_4$ can be calculated provided activity values of BO and FeO in $Fe_{1-\frac{x}{3}}B_{\frac{x}{3}}O$ solid solutions are known.

B.3 Nonstoichiometric oxides

Nonstoichiometry in oxides such as UO_2, $UO_2 - TiO_2$, PuO_2 (80, 91, 96, 103); TiO_2 (90, 101, 105); NbO_2 (85, 101, 95); MoO_2 (101) and ZrO_2 (99) have been studied using the cells of the type:

$$M\,O_{1-x}\;//\;\underset{\text{electrolyte}}{\text{Solid oxide}}\;//\;A,\,AO\;(\text{Reference electrode}) \qquad [4]$$

Reaction is

$$\tfrac{1}{2}\,O_2\,(M\,O_{1-x}) = \tfrac{1}{2}\,O_2\,(A,\,AO) \qquad (9)$$
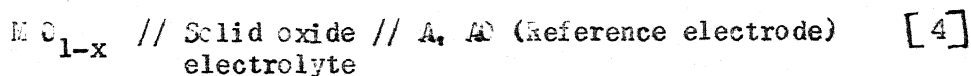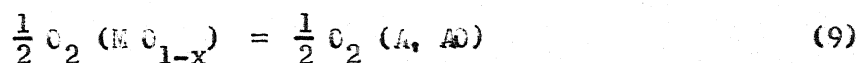
These studies are helpful in establishing the phase boundaries between the phase mixtures and single phase solid solutions of oxygen in metal oxides. The knowledge of the partial molar free energy of oxygen ($\overline{\triangle F_{O_2}}^{M}$ of FO_2) in $M - O_2$ system helps in assessing the minimum amount of contaminating oxygen

that will be present in the extractive metallurgy of various reactive metals Nb, U, V etc. Since the nonstoichiometric oxides are easily affected by cell atmosphere, the atmosphere should be extremely pure. Seperate compartment cells in which individual streams of purified gas pre-equilibrated with the electrode mixture under study have been advocated.

The nonstiochiometric oxides can be prepared by partial oxidation or reduction of stoichiometric oxides employing gas handling systems or by coulometric titration of oxygen into or out of the oxide of known composition. Coulometric titration consists of imposing an external emf on the cell so that known amount of current is passed for a certain time. From this the amount of oxygen transferred into (or out of) the nonstoichiometric electrode is known and hence new composition of the electrode can be fixed. To study narrow ranges of stoichiometry where conventional methods of gas equilibration fails, this method is extremely useful. Applicability of various defect models to these nonstoichiometric oxides can be assessed. Studies of Koch (85) and Schmalzried (106) point out to such possibilities.

C. Activity determinations in solutions of metals and oxides

C.1 Solid solutions:

  (i) Metals:

Oxygen concentration cells of the type

A, AO // Solid oxide // A - B alloy, AO   [5]
$(\mu_{O_2}^0)$ electrolyte (μ_{O_2})
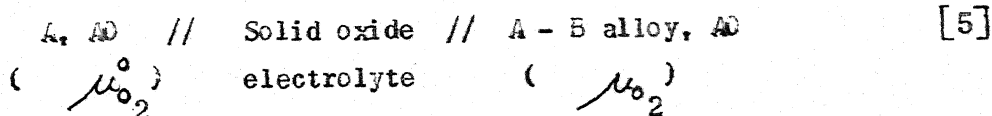
can be used for the determination of activities and phase boundaries in binary metallic solutions. Though such measurements are possible in ternary solutions, so far none have been reported.

Cell reaction: $\underline{O}$ (A-B alloy, μ_O) $= \underline{O}$ (A, AO)   (10)
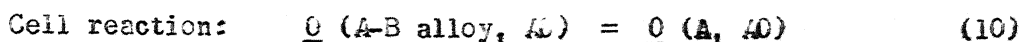
or $A = \underline{A}$ (B)

$$\mu^O_{O_2} - \mu_{O_2} = - \; n \overline{E}F \tag{11}$$

Since chemical potential of metal A is related to that of oxygen through the equilibrium constant for the formation of $AO (A + \underline{O} = A O)$, emf of the cell can be related to the activity as follows :

$$RT \ln a_A = \mu_A - \mu^O_A = \tfrac{1}{2} (\mu^O_{O_2} - \mu_{O_2}) = - \, 2\overline{E}F \tag{12}$$

By measuring the cell emf as a function of temperature and composition, activities in the binary system can be determined. From these data, various other thermodynamics properties of the system can be calculated.

For satisfactory operation of the cells, additional conditions besides the usual ones mentioned in Ch. II.1, should be met. These are noted below.

Oxygen solubility in A and AO should be as small as possible so that activity of A and AO can be taken as unity. Also, solubility of oxygen in A-B alloy should be small. If the oxygen solubility is appreciable, the activities determined would not correspond to a true binary system A-B. AO should be pure and stoichiometric. B should be more noble than A i.e. the free energy of formation of AO must be quite more negative than that of BO. It should differ by a minimum of 10 Kcals (116), so as to

avoid the displacement reaction: AO + B = A + BO

  + B · _ -. which results in compositional changes.

Solid systems Cu - Ni (112); Fe-Au, Fe-Pt, Fe-Au, Co-Au (114-121); Co-Mo, Co-pT (113); Au-Ni (120); Cu-Pt (119); Ta-W, Ta-Mo (124); Cr-Ni, Co-Pt (125) have been studied by solid electrolyte technique. Also activities of Co in Co$_3$ W (113) and Ga in Ni Ga (117) have been determined. This technique helps in determining the phase boundaries from the break in emf vs. temperature plots. Accurate estimates of solidus lines have been made in Cr-Ni and Co-Pt systems, by Fitterer et al (125) and consistency with the established phase diagrams is reported for Fe-Au and Co-Au systems by Kubik and AlCock (121).

(ii) Oxides:

The activity of oxides in solid solutions can be derived from the emf of the cell

$$A,\ AO\ //\ \begin{array}{c} \text{Solid oxide} \\ \text{electrolyte} \end{array}\ //\ A,\ \underline{AO}\ (BO) \qquad [6]$$
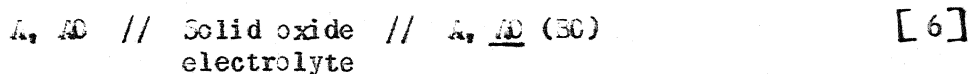
Cell reaction

$$\frac{1}{2}\ O_2\ \left[A\text{-}AO\right]\ =\ \frac{1}{2}\ O_2\ \left[A - \underline{AO}\ (BO)\right]$$

or $AO\ =\ \underline{AO}\ (BO)$ \qquad (13)

Considerations are analogous to that stated in (i) and activity of AO is given by

$$a_{AO}\ =\ \exp\ \left(\frac{-4\ \Xi F}{RT}\right) \qquad (15)$$

Activities of FeO in FeO-MgO solid solutions (115) and that of NiO in NiO-MnO and NiO-MgO (122) have been determined using this technique.

C.2 Liquid solutions

Measurements of activities in liquid solutions are comparatively few. The increased solubility of the oxygen in the liquid solutions and corrosiveness of these solutions limit the applicability of emf measurements to very few systems.

(i) Metals:

Activity determinations in liquid metals do not differ in principle from that of solid solutions. Cell assembly design is different for liquid solutions and operating temperature is fairly high. Since high oxygen solubilities contaminate the melt and affects the activity values, careful evaluation of oxygen solubility is essential. Also, suitable lead has to be chosen either for instant dipping or continuous immersion in the liquid alloy. Activities in Pb-Ni (116); Ni-Cr (123); Pb-Sn (46) systems have been determined by this technique.

(ii) Oxides:

Only activity of PbO in liquid PbO-SiO_2 solutions (46, 111) has been determined by this method. Activity measurements are possible in various other liquid silicates and PbO-MO systems, but none have been reported so far probably due to the fact that the silicates and other liquid solutions of oxide are corrosive to the electrolytes employed presently.

D. Oxygen potentials in metal melts and gas mixtures:

Oxygen chemistry forms the basis of many industrially important
metal extraction processes. Hence determination of oxygen contents and a
knowledge of thermodynamics of oxygen in various metal melts is of considerable
usefulness in exercising greater control over the metallurgical processes.
In the conventional methods of analysis of oxygen, the metal melt has to be
sampled and analysed physically or chemically for oxygen contents. In most
of the cases, the methods are time-consuming, the results are postmortem
in nature. In view of these difficulties, a probe device inserted directly
into the molten melts which could give values of oxygen instantaneously
would have obvious advantages. Electrochemical methods of measurement are
attractive because they offer this possibility. By calibrating the emf
of the cell

$$\text{Metal melt } \underline{(0)} \quad / \quad \begin{array}{c} \text{Solid oxide} \\ \text{electrolyte} \end{array} \quad / \quad \text{Reference Electrode} \qquad [7]$$
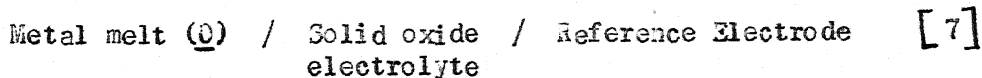
against the oxygen content measured by any one of the conventional methods,
instantenous determination of oxygen is possible. Also, the emf of the
cell [7] , gives directly the activity of oxygen in the melt. Knowing
the solubility of oxygen, activity coefficient f_M^C in the melt can be determined.
By studying the effects of various solutes on the activity of oxygen in metal
melt, interaction coefficients e_M^O can be determined. Electro-chemical
measurements of oxygen in liquid melts were reviewed by Littlewood (48),
Fisher (137 e).

D.1. Nonferrous melts:

Direct electrochemical determinations of oxygen and its
activity in the liquid metals Ag (142 - 144), Sn (134), Pb (134), Cu (136,
137 a, 140-143), dilute Ag-Cu alloys (146) were reported. Coulometric
titrations have been done (134) in liquid Sn and Pb by Bedford and Alcock
to determine the standard free energies of solution of oxygen. Fisher
et al (137 a) have determined standard free energies of solution of oxygen
by measuring the cell emf and analyzing the melt for oxygen.

D.2. Ferrous melts:

Instantaneous oxygen determination in steelmaking is of
utmost importance in various refining and controlling operations. Analysis
of various problems, methods of measurement are excellently dealt in
papers by Fitterrer et al (138); Baker & West (144); Fisher et al (137 e,
149); Pargeter (148); Fruehan & Turkdogan (151). The determination of
oxygen using solid electrolytes have also been reported by various authors
(129, 130, 133, 150). Oxygen probe consists of a disk of the electrolyte
fused to one end of quartz tube with a reference electrode inside the probe.
Emf readings stabilize within few seconds of immersion of the probe in
the melt. It has been shown (138, 148, 151) that ZrO_2 - CaO functions
adequately upto the oxygen contents corresponding to 10 PPM or more
whereas ThO_2 - Y_2O_3 electrolyte is applicable for oxygen levels of 1 PPM.
The activities of oxygen have been measured (145) in Fe, Fe-Si, Mn and
Fe-Mn melts. Effects of P, S, C, Co, Ni, Cr, V on the activities of

oxygen have been reported by Fisher et al (127).

D.3. Partial Pressures of oxygen in gas mixtures:

By determining the p_{O_2} with the help of solid electrolyte cells, $CO - CO_2$; $C-CO-CO_2$; equilibrium has been studied by Peters & Moebius (127). H_2-H_2O equilibrium in the range $1550-1750^{o}C$ was investigated by Fisher & Dieter (149). The importance of p_{O_2} measurement in various metallurgical industries was reviewed by Spacil & Schroder (55). Also p_{O_2} measurements using this technique have been reported by various authors (131, 132, 133, 139).

E. Kinetic applications:

The possibilities of solid electrolytes for kinetic applications have been reviewed recently by Rickert (53, 153), Schmalzried (54) and D.O. Raleigh (51).

Rates of deoxidation of steels have been studied (152b, 155) by observing the changes in cell emf after the introduction of various deoxidizers in the steel melt. Mass transfer studies have been done by Jakelin & Bradshaw (154). They measured continuously the concentration of oxygen in a bath of liquid silver in which a jet of oxygen gas impinged. The uptake of oxygen was continuously noted by measuring the emf with a solid electrolyte tube. Also, the rates of oxidation and reduction of various oxides FeO, Fe_2O_3, Fe_3O_4 (152a), CO_2 (152c) could be determined with the help of suitable solid electrolyte cells. In all the kinetic studies,

the reference electrode should be highly reversible for the proper

interpretation of cell emfs. The polarization behaviour of the electrodes

$Cu-Cu_2O$; $FeO - Fe_3O_4$ were studied by Iskoe & Morrell (161) to determine

the limiting currents at which the electrodes are no more reversible.

The electrochemical methods using solid electrolytes have been used in a

number of investigations of diffusivities of oxygen in various solid and

liquid metals (156 - 160; 162 - 163). Most of the measurements were done

on copper (158b, 160); Silver 156, 158b, 159) and lead (162, 163).

Consider the oxygen concentration cell

$$p'_{o2} \quad / \quad \begin{array}{c} \text{Solid oxide} \\ \text{electrolyte} \end{array} \quad / \quad p''_{o2}$$
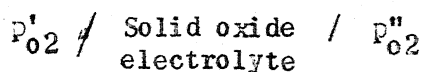
The open circuit emf gives the ratio of partial pressures of oxygen at

the two electrodes. By applying a fixed potential to above cell, a predetermined

ratio of oxygen partial pressures can be achieved. Thus, if p_{o2} is fixed at

one electrode and potential is applied to the cell, the other p_{o2} is clearly

fixed, provided the polarization is negligible. Kinetic applications are

due to the fact that the flux of current through the above cell is a measure

of the reaction rate by which oxygen is passed from one electrode to the

other. In the determinations of oxygen diffusivities in metals, the metal

is first brought into equilibrium with a fixed p_{o2} in such a way that a

known oxygen concentration is established in the metal. Then a galvanic

cell is set up with a reversible metal-metal oxide electrode (Fe-FeO) and

the metal as the other electrode.

Fe, FeO   /   Solid oxide   /   Ag (O dissolved)
                  Electrolyte

2e' $\longleftrightarrow$ $\longleftrightarrow$ $\longleftrightarrow$

O^{2-} $2\,e^{-}$
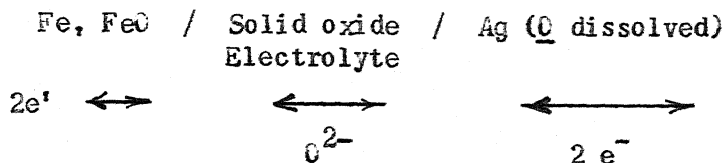
The above cell depicts the arrangement for diffusion measurement in silver by applying a potential such that oxygen concentration at the electrolyte-interface concentration is very much smaller than for Fe-FeO equilibrium, current passes through the cell in the indicated direction. This current is equivalent to oxygen diffusing out of the silver and from the knowledge of current density as function of time, and the initial oxygen concentration in silver, the diffusion coefficient of oxygen can be calculated. The method and analysis depends on the geometry employed for measurement. Linear geometry is useful for measurements in solid metals (156, 158a) whereas cylindrical geometry, in which a tube or crucible of solid electrolyte is made use of, is preferred for liquid metals (158b, 162, 163). In certain cases, the solubilities of oxygen in the solid metals can also be calculated (160).

F. Miscellaneous Applications:

Solid electrolytes have been used for analysis of nonferrous alloys (164), corrosion studies (166), and thermometry (165).

Wilder and Galin (164) have used the cell Ni, NiO/ZrO_2-CaO/Zn (in molten brass), ZnO to determine the zinc content in molten brass. In Cu-Zn-O system, the oxygen is present as ZnO and hence no ZnO has to be added separately in the right electrodes. By calibrating the emf of above

cell with zinc content in brass it has been conveniently used as an analytical tool. The error in analysis is claimed to be not more than 0.05 wt. %.

Galvanic cell of the type

Fe, FeO/Solid Oxide Electrolyte/Metal,

has been used by Mciver and Teale (166) to study corrosion of stainless Steels. The oxygen potential of slightly oxidised stainless steels at first approximates to the potential of Fe/FeO but after a short time the potential slowly decreases and becomes closer to underlying Cr/Cr_2O_3 potential.

Solid electrolyte oxygen concentration cells have also been used by Lindsay and Ruka (165) to determine high fixed point temperatures such as melting point of Ag, An and Pd on the thermodynamic scale. They have analysed various sources of error and their results within a few degrees of the accepted values for An and Ag points.

G. Future Developments:

There is considerable scope for future thermodynamic investigations of solid and liquid solutions, molten silicates and various nonstoichiometric systems by solid electrolyte galvanic cells. Phase diagram studies involving solidus or liquidus determination in new alloy systems are likely to be extended. Activity determination as in alloy systems, comprising of metals closely resembling in their electronegativities will be possible, with increased thermodynamic knowledge of oxide systems. A definite knowledge of nonstoichiometry in metal oxides and oxygen solubility in liquid alloys

will be useful for further studies of liquid alloy systems using the solid electrolyte cell technique. Interaction coefficients of oxygen in alloy systems such as e_A^O (B), e_B^O (A) can be determined if dissociation and displacement reactions in dilute solutions are negligible.

Kinetic studies involving diffusion of oxygen in solid and liquid metals and alloys; vaporization and condensation phenomenon; phase boundary reactions; reduction and oxidation characteristics of various oxides, metals; mass transfer studies between liquid metals and gases; are likely to be persued with much more vigour. With the development of suitable high temperature solid electrolyte, investigations of metallic systems at temperatures greater than 1600^OC should be possible. Analytical studies such as oxygen determination in ferrous and nonferrous alloys, determination of the amount of reactive metal component in various liquid alloys will be persued further. A variety of thermodynamic and kinetic studies will be possible with the development of new electrolyte systems, other than oxides, such as carbides, nitrides, sulphides and borides.

CHAPTER III

PLAN OF THE WORK

A. Previous work on copper-silver system:

Thermodynamic properties of liquid copper-silver alloys have been determined in the past by employing three methods, calorimetry (1, 6), vapor pressure measurement (3) and distribution equilibria (5). Phase diagram calculations have also been carried out (8).

Earliest calorimetric determinations of heats of formation of liquid copper-silver alloys for mole fraction of copper $(X_{Cu}) = 0.22 - 0.8$, were done by Kawakami (1) in 1930. The more recent calorimetric measurements were done by Oriani and Murphy (6a) and Dakken and Elliott (6b). Oriani and Murphy investigated the compositional range $X_{Cu} = 0.1$ to 0.8 at $1373^{\circ}K$, whereas Dakken and Elliott's investigations were confined to copper rich alloys, $X_{Cu} = 0.6 - 0.9$ at $1373^{\circ}K$. Kawakami's measurements were found to be inaccurate and there is good agreement between the values of the latter investigators.

Edwards and Downing (3) measured the vapor pressures of silver and copper over liquid Cu-Ag alloys for $X_{Cu} = 0.14 - 0.95$, in the temperature range $1300-1560^{\circ}K$, by effusion cell technique. Activities were calculated at each temperature and the properties have been reported at the mean temperature of $1428^{\circ}K$. Hultgren (8) points out quite a few thermodynamic inconsistincies in Edwards and Downing's values. The activities of silver

show an increase in scatter as the mole fraction of silver (X_{Ag}) goes up and at $X_{Ag} = 0.66$, the scatter is 10% of the mean value. Activity of silver (a_{Ag}) does not merge into Raoult's law line when X_{Ag} tends to unity. Also the values of partial molar free energy of silver (F_{Ag}^M) extrapolated to liquidus temperatures are found to be positive, when referred to solid silver as the standard state. Finally, F_{Cu}^M values derived from copper vapor pressures show a wide scatter.

Koros and Chipman (5) measured activity of copper (a_{Cu}) in liquid iron at 1873^0K by equilibrating with Ag-Cu alloy. For this purpose they made phase diagram computations of γ_{Cu} in Ag using the measured heats of mixing of Kawakami at 1200^0K. The terminal solid solutions are assumed to obey Raoult's law and the excess values of mixing of components in the liquid phase is obtained by an equation given by Wagner (13).

Hultgren et al (8) in their thermodynamic compilation, have critically reviewed these studies and reported the selected values for Ag-Cu system. They preferred the values of Oriani and Murphy for heats of mixing in liquid alloys. Assuming the thermodynamic properties of Cu-Fe system as correct, the selected values of F_{Cu}^M in the range $X_{Cu} = 0.01-0.12$ were calculated from the measurements of Koros and Chipman. In the compositional range $0.12 < X_{Cu} < 0.4$, F_{Cu}^M values were interpolated so that subsequent Gibbs-Duhem integration would yield a value of F_{Ag}^M at the eutectic point which was consistent with the properties of solid phases. The selected properties of liquid alloys in this range are not consistent with the properties of α phase, liquidus and solidus temperature.

Hence more accurate determinations on the thermodynamics of liquid alloys and phase diagram, are needed in this range.

B. Plan of the present work:

The preceding discussions clearly point out the need for more precise determinations in the liquid Cu-Ag alloys. Therefore, direct measurements of activity were planned in this system by solid electrolyte galvanic cell method. Various investigators have demonstrated emf measurements with the solid oxide electrolyte are capable of yielding results with good accuracy. In the present work, the cell was

$$Cu(S), \; Cu_2O(S) \; // \quad CaO - ZrO_2 \quad // \; Cu\text{-}Ag \text{ alloy (1)}, \qquad [1]$$
$$\text{Solid Electrolyte} \qquad Cu_2O(S)$$
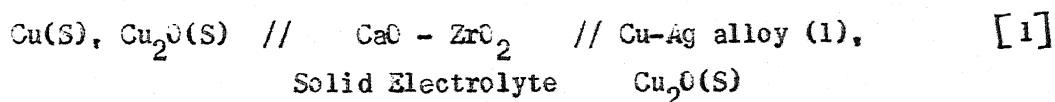
This type of cell has been employed by Cavanaugh and Elliott (116) and Goto and St. Pierre (126) for activity determinations in liquid alloys, and is of the general type A, AO // Solid oxide // A-B alloy, AO   [2]
Electrolyte

Such cells yield activity values of A in the alloy A-B directly from the cell emf's. In cell, if $p_{O_2}^{o}$ and p_{O_2} are the partial pressures of oxygen in equilibrium with Cu and Cu_2O, on the left and right sides of the electrolyte, then

$$E = \text{Emf of the cell} = \frac{R\,T}{4\,F} \; \ln \frac{p_{O_2}}{p_{O_2}^{o}} \qquad (1)$$

Again, $4 \, Cu \, (S, \text{ or in alloy}) + O_2 \, (g) = 2 \, Cu_2O \, (S)$ \qquad (2)
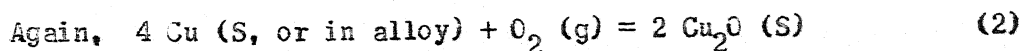
$$K = a^2_{Cu_2O} / (a^4_{Cu} \times p_{O_2}) \qquad (3)$$

If Cu_2O is pure, $$p_{O_2} = \frac{1}{K \cdot a^4_{Cu}} \qquad (4)$$

Taking the pure solid copper as the standard state and combining equations, we obtain

$$E = -\frac{RT}{F} \ln a_{Cu} \qquad (5)$$

or $$F^M_{Cu} = -EF \quad \& \quad S^M_{Cu} = -\frac{F^M_{Cu}}{dT} = F\left(\frac{dE}{dT}\right) \qquad (6)$$

Gibbs-Duhem integration can yield partial thermodynamic properties of silver. From these partial values, integral and excess values can be calculated in the usual manner.

To employ solid electrolyte cell technique, the requirements enlisted in Ch. II, have to be satisfied. The calcia-stabilized zirconia is a perfect ionic conductor (47) in the range of p_{O_2} prevailing during the experimental conditions ($p_{O_2} > 10^{-10}$ atoms). Cu_2O is much more stable than Ag_2O and hence p_{O_2} at each electrode is dictated by Cu (S or in alloy) - Cu_2O equilibrium alone. The difference of standard free energies of formation ($\triangle F^o$) of Ag_2O and Cu_2O is of the order of 60,000 cals. Therefore, the formation of Ag_2O in the melt is not possible and the displacement reaction $Cu_2O + 2\underline{Ag} = 2\underline{Cu} + Ag_2O$ cannot take place. Cu_2O exhibits little non-stoichiometry in the experimental temperature range of 760-1050°C. This is evident from the Cu-O phase diagram given in Hansen (4). Above 1230°C, Cu_2O decomposes into Cu_2O and O_2. Upto approximately 1065°C,

almost pure solid copper will be in equilibrium with solid Cu_2O. Above 1065^0C, Cu_2O will be no longer in equilibrium with pure copper but with liquid Cu and a few percentage of oxygen dissolved. Hence the upper temperature limit for the successful operation of the cell would be 1060^0C. Thus, a temperature range of 100 to 250^0C is possible in this investigation. Except in predominantly copper-rich or silver-rich alloys, the temperature coefficients of the cell would be fairly reliable and thermodynamic properties of liquid copper-silver alloys can be found out. Oxygen solubilities in pure Cu and Cu-Ag alloys to be investigated must be as small as possible. Otherwise the system under study would be a ternary system Cu-Ag-O and the oxygen may have strong influence on the activity values of copper. Below 1050^0C, there is negligible solubility of oxygen in solid copper. Since oxygen solubility data on Ag-Cu alloys is lacking, preliminary estimate was made from Tankin & Belton's (22) model. This model permits the estimation of solubilities in binary metallic alloys from the energies of solution of oxygen in the component metals. Calculations based on this model revealed that solubility is nearly 1 atom percent for $X_{Cu} = 0.15$. Thus Cu-Ag system satisfies most of the requirements for the solid electrolyte galvanic cell measurements.

The work was planned in three parts.

(i) <u>Calibration run</u>:   A galvanic cell with known emf and the

$$Cu, \ Cu_2O \ // \ \text{Solid Electrolyte} \ // \ Ni, \ NiO \qquad [3]$$

measured emf can be compared with precise values of this cells that are available in literature. Good match between the observed and actual values would establish the soundness of the electrolyte and the cell geometry employed i.e. absence of electronic conductivity in the electrolyte, negligible gas transport between the two electrode compartments.

(ii) <u>Selection of lead for the liquid alloys</u>: Dissolution of the lead in the liquid alloy is a serious problem in this kind of studies. Hence trial runs using various leads have to be taken to establish the right kind of lead to be employed for immersion in liquid Cu-Ag alloys. Ta, Mo, inconel, Cu_2O coated Cu, Cu_2O and cermets were possible choices of lead wires.

(iii) <u>Experiments on copper-silver system</u>: Taking all the preceding considerations into account, it was decided to investigate the compositional range, X_{Cu} = 0.1 to 0.9 between $1050^{o}C$ and liquidus temperature of the alloy.

CHAPTER IV

APPARATUS AND EXPERIMENTAL TECHNIQUES

A. Furnace and Reaction Tube:

The furnace used was a vertical globar furnace in which the six globars equally spaced from the center served as heating elements. The furnace was designed to operate upto a maximum temperature of $1400^{\circ}C$. After the furnace was set in operation, temperature profile was taken and length of constant temperature zone was found to be at least 1½". Power to the furnace was supplied from a voltage stabilizer, connected straight to the mains.

The reaction tube was of mullite (O.D $2\frac{3}{4}$", I.D 2½", Ht. 20"), fitted with two brass heads at either end Brass heads contained grooves in which silicone rubber gaskets could be tightly fitted. Brass heads could be rigidly clamped to the reaction tube, the ends of which pressed against the groove and made it gas tight. Bottom brass head was sealed permanently with white RTV silicone sealant. Purified argon could be introduced into the furnace through a port in the bottom brass head. Top brass head had individual ports for thermocouple sheaths, lead wires, addition tube and argon outlet tube. Stainless tubes brazed to the brass head acted as guide tubes. Around the periphery of top brass head, a single round of copper tubing was soldered to it and water could be continuously circulated through the tubing to keep the head cool. A peep hole covered with blue glass was

provided in the brass head to assist in viewing the cell assumbly.

B. Temperature : Control and Measurement:

The temperature of the furnace could be controlled within $\pm 1^{\circ}C$ using electromax signalling controller coupled to a relay mechanism and a chromel-alumel thermocouple. The thermocouple with a double bore alumina sheath was placed right in the center of the furnace through a hole drilled across the furnace shell. The temperature of the inside cell assumbly was independently measured by a calibrated platinum-platinum/10% rhodium thermocouple using Leeds and Northrup potentiometer - model 8686.

C. Emf Measurement:

A potentiometer assembled in the laboratory was used for emf measurements.

     Specifications: Galvanometer-2435 series, Reflection type sensitivity - 0.025 microamperes per scale division. Potentiometer - model 7645

Galvanometer and Potentiometer were Leeds and Northrup make.

D. Gas Train:

Argon was purified by successively passing it through a copper-gauge furnace maintained at $550^{\circ}C$, series of $CaCl_2$ and P_2O_5 towers and finally through magnesium-chip furnace at $500^{\circ}C$. Copper gauge and magnesium chip furnaces were of resistance wound type and were designed

in the laboratory. Copper and magnesium act as oxygen getters while $CaCl_2$ and P_2O_5 absorb the traces of moisture in argon. During the experiments, stream of purified argon at slow flow rate was maintained in the furnace chamber. Slight positive pressure was maintained inside the furnace. The flow rate could be visually inspected as argon flows through the bubblers at the inlet and outlet ends.

E. Experimental Materials:

Following materials were used in the cell set up.

1. Solid electrolyte crucible - $\frac{3}{8}$" I.D, ½" O.D, 1" high 15 mole percent calcia-stabilized zirconia. Supplied by Zirconium Corporation of America.

2. ZIRCOA - B powder - Zirconia fully stabilized with calcia(- 325 mesh)

3. Nickel and copper - Semi elements inc. U.S.A., Purity greater than 99.97%

4. Silver - American Smelting and Refining Co., U.S.A.; Purity 99.99%

5. Platinum and Pt-10% Rh - Baker Co., U.S.A., Thermocouple and commercial grade

6. Cuprous oxide and Nickel oxide - Fisher certified reagents

7. Metamic 612 cermets - Approximately contains 72% Cr, 20% Al_2O_3, rest silica and other constituents; Morganite Ltd.,

8. RTV silicon sealant - white (Pourable) GEC.

F. Cell Assembly:

The cell consists of solid electrolyte in contact with two electrodes on either side of it. Two types of cells as shown schematically in Fig. 1a and b were employed in the present work.

In cell a, the electrolyte was 15 mol % Calcia stabilized zirconia crucible and the reference electrode was finely ground mixture of copper and cuprous oxide. The electrolyte crucible served as the container. recrystallized alumina crucible or a laboratory made zirconia crucible was used as the container for the test electrode Cu-Ag alloy and Cu_2O.

In cell b, laboratory made crucibles from fully stabilized ZIRCOA-B powder, served as the electrolyte. The crucibles were slip-cast, presintered at $1200^{\circ}C$ for one day and finally sintered at $2000^{\circ}C$ for 6 hrs. in ZIRCOA pot furnace. Further details of crucible preparation are given in Appendix - C. Thin copper foil was wrapped around the electrolyte crucible and the annular gap was filled with $Cu-Cu_2O$ mixture. The test electrode of Cu-Ag alloy with Cu_2O was placed inside the electrolyte crucible. The electrolyte crucible was placed inside a recrystallized alumina or another zirconia crucible with Cu shots along with Cu_2O is placed in the outer crucible to promote local equilibrium.

The whole cell assumbly was placed in a silica crucible (O.D $1\frac{7}{8}$", 4" height), resting on the supporting mullite tube. It was ensured that cell assembly was in the constant temperature zone.

(b)

1. Recrystallized alumina crucible
2. Solid electrolyte crucible
3. Quartz tube for addition
4. Thin copper foil
5. Cu-Cu$_2$O reference electrode
6. Cu-Ag melt with Cu$_2$O
7. Cu shots with Cu$_2$O
8. Double bore Alumina sheath
9. Alumina guide tubes for lead wires
10. Platinum lead wires
11. Cermets

(a)

1. Reaction Tube – Mullite
2. Supporting Mullite tube
3. Outer Silica Crucible
4. Recrystallized Alumina Crucible
5. Double bore alumina sheath for Pt/Pt-Rh thermocouple
6. Addition tube – Quartz
7. Alumina guide tubes for lead wires
8. Platinum lead wires
9. Cermets
10. Solid electrolyte crucible
11. Cu-Cu$_2$O Reference electrode
12. Cu-Ag melt with Cu$_2$O
13. Purified Argon from gas train

G. Leads:

Considerations of the lead for liquid alloy were already discussed under Ch. II. In this study Cu coated with Cu_2O, Inconel, cermet and sintered Cu_2O were tried as lead wires. Cu was partly oxidized to Cu_2O and trials carried out with this lead revealed that there was considerable dissolution of underlying Cu, even with instant dipping. Next, inconel was tried and in this case also dipping of the lead in the alloy was momentary. Two compositions of the alloy were studied using inconel as lead. Except for the difficulty of lowering down the lead into the melt, everytime a measurement was taken, inconel seemed to be a satisfactory lead wire. Though an oxide coating was observed on inconel, it did not affect the results. The emfs measured with inconel were reproducible and reversible. To eliminate thermal emf's, inconel was used as lead form both the electrodes. The lead for Cu-Ag alloy was just placed above the melt when measurements were not taken. During the time of measurement, it could be pushed easily due to the elasticity of silicone scalant placed in the annular gap of the inconel lead and the alumina sheath. It was observed that inconel could be dipped in the melt at least for a minute without affecting the results.

The third trial was done with a chromium based cermet, similar to the one used by Diaz and Richardson(143). Advantages of cermet lie in the fact that they can be immersed continuously and make the experimentation easier. The cermet got superficially oxidized but this did not affect the cell emf. The potentials measured with the help of cermet proved to be quite

reversible. In view of the large oxygen potential difference between Cr_2O_3 and Cu_2O, negaligible amount of chromium from the cermet is expected to dissolve. Diaz and Richardson's (143) analysis of copper-oxygen melts in contact with the cermet for 10 days at $1100^\circ C$ revealed that .02% Cr has dissolved. The cermets were hanged by platinum wires and they were kept in position by tying them to the alumina guide tubes or closely fitting them in the alumina tube, as shown in Fig. 1. Most of the runs were taken with the cermets.

Sintered cuprous oxide (Cu_2O) in the form of thin rod was also tried as lead. Fine Cu_2O powder was packed tightly in one end closed quartz tube and a platinum wire was placed in the powder. Cu_2O was isintered on to the platinum wire by heating the quartz tube to $1000^\circ C$ for about 10 hrs under argon atmosphere. Quartz tube was gently broken so as to cause little damage to the sintered rod. The positioning of this lead in the cell was similar to that of cermet and gave reproducible and stable values of emf's.

E. Calibration runs:

The cell a was used in most of the runs. In order to make sure that there was no significant gaseous transport via atmosphere and electronic conductivity in the electrolyte, a calibration run was taken with mixtures of $Cu-Cu_2O$ and Ni-NiO as the two electrodes.

The electrode mixtures were prepared by thoroughly grinding the metal-metal oxide powders in an agate mortar. $Cu-Cu_2O$ mixture was packed inside the electrolyte crucible upto half of its height. The contact to

this reference electrode was established by pressing a platinum disk, which was spot-welded to Pt and Pt/10% Rh wires, sheathed in a double bore alumina tube. This served as lead as well as thermocouple. Platinum wire was wound round the electrolyte crucible and a moist paste of Ni-NiO was applied over it. This platinum wire was sheathed in a single bore alumina tube and served as the lead from the test electrode. The electrolyte crucible was placed inside a recrystallized alumina crucible containing Ni-NiO mixture so as to promote local thermodynamic equilibrium. The alumina sheaths carrying lead wire and thermocouple wires were brought out of the furnace by passing them through the stainless tubes of brass head and it was tightly clamped to the reaction tube. All the openings in the brass head were closed using the sealant and the furnace chamber was made gas tight.

The furnace chamber was first flushed with purified argon and then slowly heated to 200°C. The temperature was maintained at 200°C for about 2 hrs and the moisture from the moist paste of Ni-NiO was evacuated and flushed out with argon repeatedly. Then the furnace was slowly heated to 900°C in about 8 hrs under a slow flow of purified argon. Both the electrode mixtures got sintered 'insitu' establishing very good electrical contact. The duration of the run was about one week and the temperature cycling was done two times in the range 750 to 1050°C. Below 750 and above 1050 the cell emf's were not reproducible. The cell was allowed to equilibrate at the desired temperature and the measured emf was considered as equilibrium one, if it remained constant within $\pm$ 0.2 mV for a minimum period of 6 hrs.

Usually the temperature setting was left unchanged for at least 8 hours.
Also, the cell was left overnight and at times for one full day at
arbitarily selected temperatures. The emf's remained steady and the
fluctuations were always within 0.5 mV. Only during the end of the run
(on 8th day), cell deteriotated and the run was abandoned. During the emf
measurements, reversibility tests were administered. Flow rates were varied
between 15 bubbles per min. to 150 b/m at least twice a day. No adverse
effect was noticed on the cell and the emf remained steady ($\pm$ 0.2). The
reversibility was also tested by imposing emf on the cell from an external
source in either direction, and observing the behaviour of the system. The
emf approached equilibrium value within half an hour of the polarization
and took maximum of two hours to become steady. The calibration run results
are presented in the Appendix-A and these values are compared with the
precise values available in the literature in Table I and the agreement was
excellent.

The cell b was calibrated against cell a by measuring the emf vs.
temperature relation for the same alloy (X_{Cu}=0.5) in both the cases. The
emf's from a & b cells matched within 1 mV and hence it was concluded that
cell b was also good for measurements on liquid alloys.

I. Experiments on Cu-Ag system:-

The master alloys of copper and silver were prepared by melting
the required amounts of these metal shots either in evacuated and sealed
quartz tubes or in one end open quartz tube under a stream of purified argon.

Weight of each master alloy ranged between 7 and 10 grams. The alloys were taken in the recrystallized alumina crucible (cell a) or in the electrolyte crucible (cell b) along with 1 to 2 gms. of Cu_2O. The whole cell assembly with the leads in position was encased in the silica crucible and was lowered into the furnace.

After making the furnace chamber gas tight, it was flushed with argon and evacuated around 150^0C with the cell assembly in position. It was filled with argon and then slowly heated to 1000^0C in about 9 hrs. At this temperature, the cell used to attain equilibrium in less than two hrs. Emf's were recorded at intervals of 30 minutes and if the variation was within $\pm$ 0.1 mV in a period of 2 hrs, the values were considered to be equilibrium ones.[6] Almost instantaneous response was noticed in the all emf's whenever temperature changes were effected. In all the runs, the stability of emf with time was tested by leaving the cell undisturbed for at least 6 hrs. The variations in emf never exceeded 0.5 mV. Changes in gas flow rates did not affect the results. The reversibility of the cell used to be checked by polarizing it in both directions. Even after heavy polarization (1 memp for 3 mts.), emf's approached the equilibrium value within 5 mts. and usually a maximum of 30 minutes were enough for attainment of steady emf's.

In the same run, more than one composition could be studied by appropriation additions of the metal shots through the quartz addition tube filled with a removable cap at the top. It was held ½" above the melt by

sealing it to the stainless steel tube with the silicon sealant. Addition time was kept to minimum and during this period high flow rate of argon was maintained to avoid any possible oxidation of the alloy. Immediate changes in emf's upon addition were observed and steady emf's used to be attained in about 2 hours time.

Chemical analysis of the alloys were not done. In order to make sure of the constancy of the compositions during the runs, a few times the same compositions were obtained either directly from master alloys of additions. Emf's by these two procedures differed by less than 1 mV. This observation coupled with the fact that, the temperature cycling yielded reproducible emf's and the emf vs. temperature plots were essentially linear with standard deviations of less than 1 mV in all the runs, pointed out to the negligible compositional changes during the runs either through evaporation of silver or in any other possible manner.

CHAPTER V

RESULTS and DISCUSSIONS

A. Results:

The measurements were mainly confined in the range of X_{Cu}=0.1-0.6

and in the temperature T liquidus to 1330^{0}K, A few measurements were done

below the liquidus temperature and above 1330^{0}K. Though the compositions

X_{Cu} = 0.25 and 0.9 were studied, it was felt that the measurements were

not precise enough to derive the various thermodynamic properties and hence

they were not considered. Nevertheless, cell emf as a function of temperature

for all the compositions investigated are given in the Appendix-A.

A computer programme was developed to derive partial molar values

of copper from the basic emf data of the cell. This programme can be

modified to derive all the thermodynamic properties of alloys in certain

limiting cases. Firstly, least square linear relationships were fitted

between emf and temperature, then, activities (a_{Cu}); activity coefficients

(γ_{Cu}); partial molar values of free energy, entropy and enthalpies of

mixing (F^{M}_{Cu}, S^{M}_{Cu}, H^{M}_{Cu}); Alpha functions (α_{Cu}) and Beta functions (β_{Cu}) of

copper were calculated from the cell data. The program used is presented

in the Appendix-B.

The cell emfs give partial quantities for copper directly with

solid copper as the standard state. For interpretation of thermodynamic

properties of liquid alloys, standard state of pure liquid metal is pre-

ferrable. Hence, the liquid copper was employed as the standard state by

making appropriate corrections for fusion values of copper. The partial
quantities of copper are calculated using the following equations.

$$F_{Cu}^{M} = - \mathcal{F} + \Delta F_{fusion} = RT \ \ln a_{Cu} \qquad (1)$$

$$S_{Cu}^{M} = F \ \frac{d\mathcal{F}}{dT} - \Delta S_{fusion} \qquad (2)$$

$$H_{Cu}^{M} = F_{Cu}^{M} + T \ S_{Cu}^{M} \qquad (3)$$

In the experimental range of temperature, H_{Cu}^{M} and S_{Cu}^{M} are considered as
constant. The partial thermodynamic quantities for silver can be determined,
with liquid copper as the standard state using the following equations

$$\log a_{Ag} = \log X_{Ag} - X_{Ag} \ X_{Cu} \alpha_{Cu} + \int_{0}^{X_{Cu}} \alpha_{Cu} \cdot d \ X_{Cu} \qquad (4)$$

$$F_{Ag}^{M} = 4.576 \ T \log a_{Ag} \qquad (5)$$

$$H_{Ag}^{M} = - X_{Ag} \ X_{Cu} \beta_{Cu} + \int_{0}^{X_{Cu}} \beta_{Cu} \cdot d \ X_{Cu} \qquad (6)$$

$$S_{Ag}^{M} = (H_{Ag}^{M} - F_{Ag}^{M})/T \qquad (7)$$

where,

$$\alpha_{Cu} = \log \gamma_{Cu}/(1 - X_{Cu})^2 \qquad (8)$$

$$\beta_{Cu} = H_{Cu}^{M}/(1 - X_{Cu})^2 \qquad (9)$$

The integrals in the equations (4) and (6) have been evaluated
graphically from Figs. 4 and 5. From these partial values, integral and excess

molar properties of mixing are calculated as follows.

$$F^M = X_{Cu} F^M_{Cu} + X_{Ag} F^M_{Ag} \qquad (10)$$

$$H^M = H^E = (1 - X_{Cu}) \int_0^{X_{Cu}} \beta_{Cu} \cdot d X_{Cu} \qquad (11)$$

$$S^M = (H^M - F^M)/T \qquad (12)$$

where F^M, H^M, S^M are integral molar free energy, enthalpy and entropies respectively. F^E, S^E are excess molar properties and can be evaluated using

$$F^E = (1 - X_{Cu}) \int_0^{X_{Cu}} \alpha_{Cu} \cdot d X_{Cu} \qquad (13)$$

$$S^E = (H^M - F^E)/T \qquad (14)$$

B. DISCUSSION:

Emf versus temperature plots for $X_{Cu} = 0.1$ to 0.6 are shown in Fig. 2. Table II presents the results analytically, along with the standard and maximum deviations. Details of cell and leads employed are clearly depicted in Fig. 2. The emfs have been extrapolated to 1400°K, after correcting for $\frac{dE}{dT}$ at the melting point of copper (1356°K). Since the range of extrapolation is small (about 70°), the extrapolation is justified. The extrapolated values at 1400°K are useful in comparing the values of this work with the selected values reported by Hultgren et al (6). The cell data are independent of the geometry and the leads employed. They

were unaffected by the changes in gas flow rates and polarization tests showed excellent reversibility. Stray emfs were not encountered, since the same emfs were obtained irrespective of whether the furnace supply was on or off. Emfs were measured below liquidus for a few compositions only. Hultgren et al (8) give a value of 0.96 ± .005 for the activity of copper at the eutectic temperature (1052°K). The emf data at the eutectic composition $X_{Cu} = 0.4$ and $X_{Cu} = 0.7$ yielded values of 0.953 and 0.965 respectively. This agreement is considered quite good. The emf for $X_{Cu} = 0.7$ near the eutectic temperature is not shown in Fig. 2 but the value is reported in Appendix - A. At $X_{Cu} = 0.1$, the liquidus determined is 13°C higher than that interpolated from the phase diagram. Repetition with another master alloy of same composition, yielded reproducible results. At $X_{Cu} = 0.2$ and 0.3, considerable supercooling (greater than 20°K) was observed. Even prolonged equilibration (12 to 18 hours) and stirring of the bath resulted in the same emfs. The dissolved oxygen could be the cause for the lowering of liquidus at $X_{Cu} = 0.2$ and 0.3. But the higher liquidus at $X_{Cu} = 0.1$ can not be explained in the absence of chemical analysis of the alloy for oxygen and copper contents of the alloy.

The activities of copper and silver at 1200°, 1300°, 1400°K (extrapolated) are presented in Fig. 3 and Table III along with the values reported by Hultgren et al (8). The standard states for both are pure liquid metals. For determination of activity of silver, extrapolated value of α_{Cu} was employed only for $X_{Cu} = 0.8$, since at this composition

γ_{Cu} is close to unity and a little error in a_{Cu} can lead to a large uncertainity in α_{Cu}. The extrapolated values at $1400^{o}K$ are 10 to 15% higher on silver rich side and 3 to 5% lower on high copper side, compared to those of Hultgren et al (8).

As Table IV shows H_{Cu}^{M} obtained from the intercepts of emf versus temperature plots increase with decreasing X_{Cu}, except at $X_{Cu} = 0.1$, where it is unusually low. The large change in solubility of oxygen with temperature could be causing the discrepancy. Quantitative explanation could not be given in the absence of oxygen solubility data in these alloys. If Cu_2O will dissolve in the liquid alloy according to the reaction,

$$Cu_2O \ (S) \ = \ 2 \ \underline{Cu} \ + \ \underline{O} \tag{15}$$

it can lead to an increase in X_{Cu} by fraction of few hundredths, which is enough to decrease the slope of emf versus temperature plot and hence decrease measured E^{M} considerably. This process is reversible with temperature and hence temperature cycling will not reveal any irreproducibility. Approximate calculations on the basis of model proposed by Belton and Tankins (22) for the solubility of oxygen in binary alloys, confirms that oxygen solubility is nearly 1 atom % at $1300^{o}K$ for silver rich alloys ($X_{Cu} = 0.15$). The detailed procedure of estimation is shown in the Appendix - D. Using the standard free energies of solution oxygen in copper and silver and the equilibrium p_{O2} over Cu-Ag alloys with Cu_2O, the solubility of oxygen in the alloys can be calculated. These calculations are qualitative in nature and hence serious deductions cannot be made unless precise oxygen solubilities

and its effect on the activity of oxygen are known. The inaccuracy in the activity of copper at $X_{Cu} = 0.1$, from the slope changes of Emf - temperature plots, due to changes in oxygen solubility is estimated to be not more than 3% at $1300^{\circ}K$. For $X_{Cu} = 0.2$, the dissociation of Cu_2O will not cause appreciable compositional changes (less than .005 in X_{Cu}). Moreover, the emf values for the alloys are much less sensitive to slight compositional changes and the resulting changes in H_{Cu}^{M} will be well within the experimental uncertainity. Even if an approximate correction for oxygen solubility, could be made in a_{Cu} values for $X_{Cu} < 0.4$, our values seem to be higher than the values reported by Hultgren et al (8). Integral and excess molar free energies of mixing (F^{M} and F^{E}) of this work are compared with those of Hultgren et al (8) in Fig. 6 and the agreement is quite good.

Extrapolated values of β_{Cu} were preferred at $X_{Cu} = 0.1$ and 0.8. At $X_{Cu} = 0.8$, β_{Cu} is very much sensitive and an uncertainity of .005 in the temperature coefficient of the cell emf will lead to a large error in H_{Cu}^{M} and β_{Cu}. As Fig. 7 shows, our values for integral molar heats of mixing H^{M} agree well with calorimetric values (1, 6) in the high Cu range, whereas in the lower copper side, our values are somewhat lower. Considering the uncertainity of nearly 200 cals in H^{M} values of present work, the agreement is good.

Uncertainity analysis of the various thermodynamic quantities were performed for a typical composition $X_{Cu} = 0.5$ at $1300^{\circ}K$. The various uncertainities are shown in brackets in Table IV. The detailed procedure of uncertainity estimates is given in Appendix - E.

CHAPTER VI

SUMMARY and CONCLUSIONS

Liquid copper-silver alloys were investigated using solid electrolyte cell technique. From the basic cell emf data, various thermodynamic functions of liquid copper-silver alloys for $X_{Cu} = 0.1 - 0.8$ were determined and reported at a temperature of $1300^{\circ}K$. The thermodynamic values of this work extrapolated to $1400^{\circ}K$ were compared with the selected values of Hultgren et al (8). The activity data obtained from this work are considered to be more accurate than the previous data. The calculated integral heats of mixing from the emf and the temperature coefficient of the cell, agree with the recent accurate calorimetric determinations within the experimental uncertainity. At few compositions, graphically extrapolated values of Alpha and Beta functions were preferred rather than the experimental values, as these are subjected to serious errors despite small uncertainities in cell emf data. The liquidus temperatures determined for few compositions of silver-rich alloys do not match with those of phase diagram. The oxygen solubility in copper-silver alloys is thought to be one of the main reasons for the above discrepancy. For accurate estimation of entropies of mixing, the accurate activity values of this work should be combined with the precise heats of mixing values from calorimetric work.

CHAPTER VII

SUGGESTIONS FOR FURTHER WORK

Further work on Cu-Ag system consists in accurate determination of liquidus temperatures and the effect of oxygen solubilities on the liquidus solid Cu-Ag alloys can also be investigated by this technique to establish the solidus of the system accurately. If the oxygen solubilities are compatible with the solid electrolyte cell requirements, activities in binary Cu-Au and ternary Cu-Ag-Au systems can be investigated. Activity of oxygen in dilute $Cu - X - O$ systems can be determined by emf method to understand the thermodynamics of oxygen in dilute solutions and for model studies in these solutions. Coulometric titrations are convenient means for the determination of activity coefficients and interaction coefficients and can be used to determine these thermodynamic quantities in $Cu - X - O$ solutions. Also, activity calculations of Cu_2O can be made in $Cu_2O - XO$ systems such as $Cu_2O - PbO$ by emf technique. Kinetic studies such as oxygen diffusivity determinations in $Cu - X$ solutions are possible.
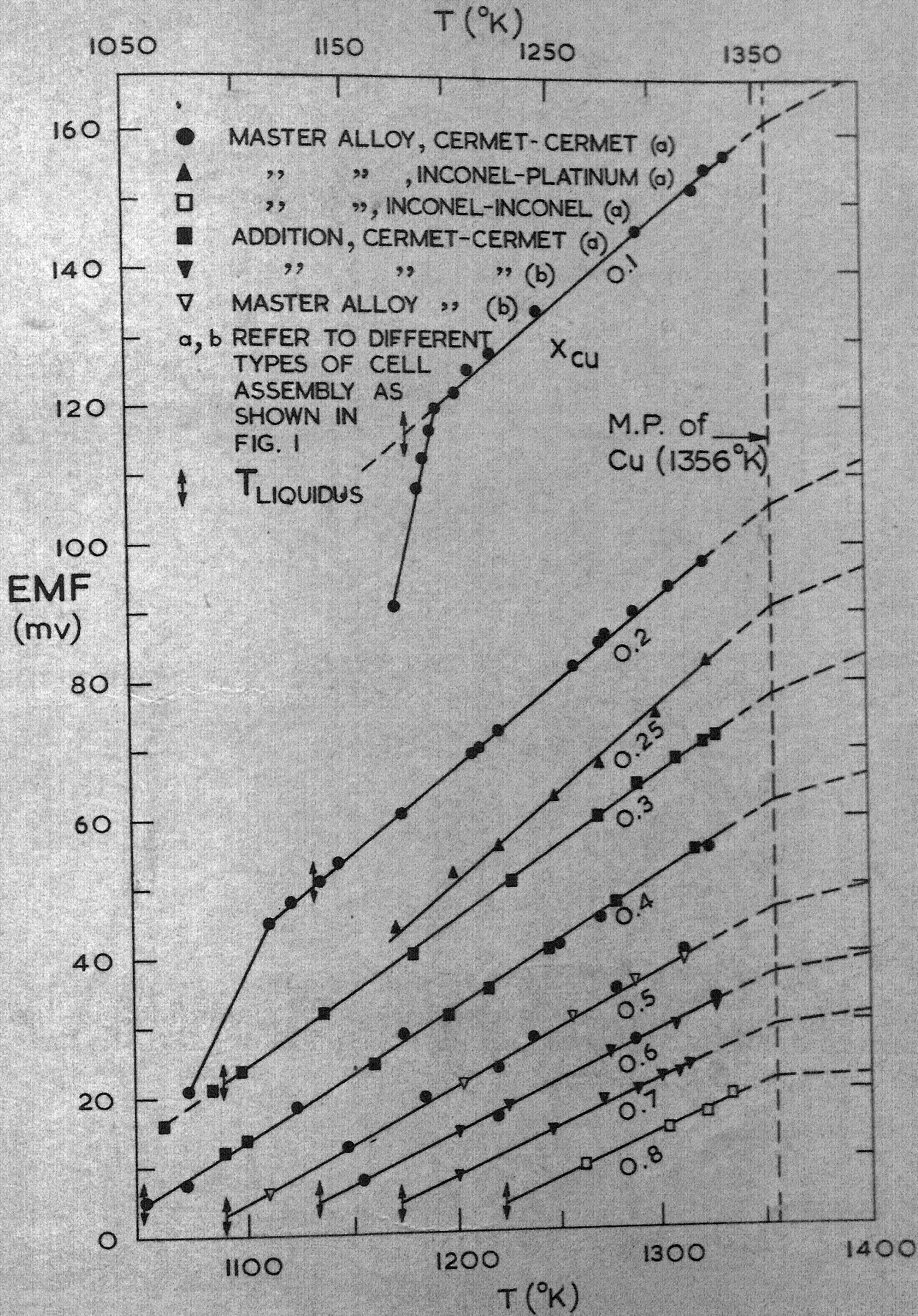
FIG. 2
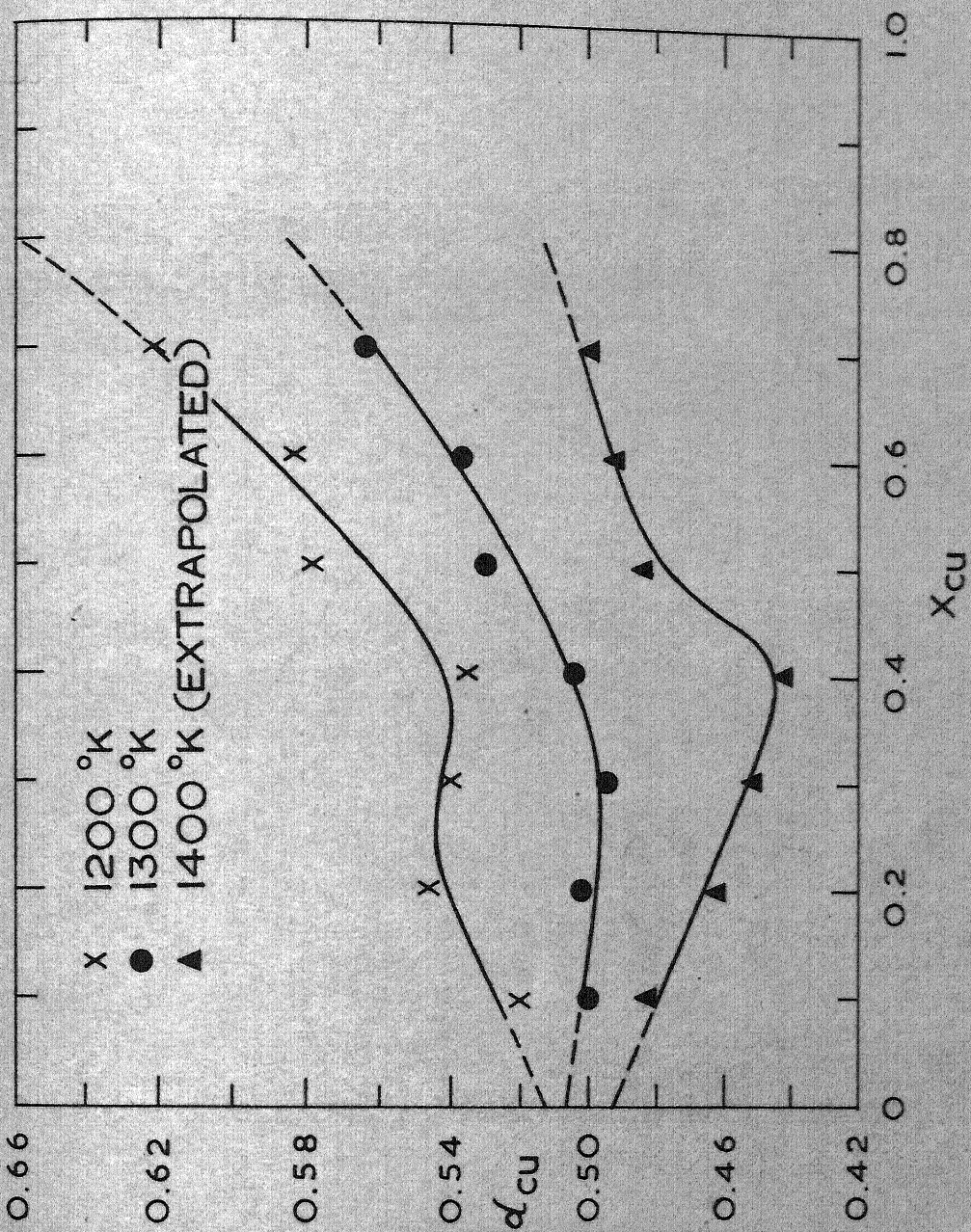
FIG. 4
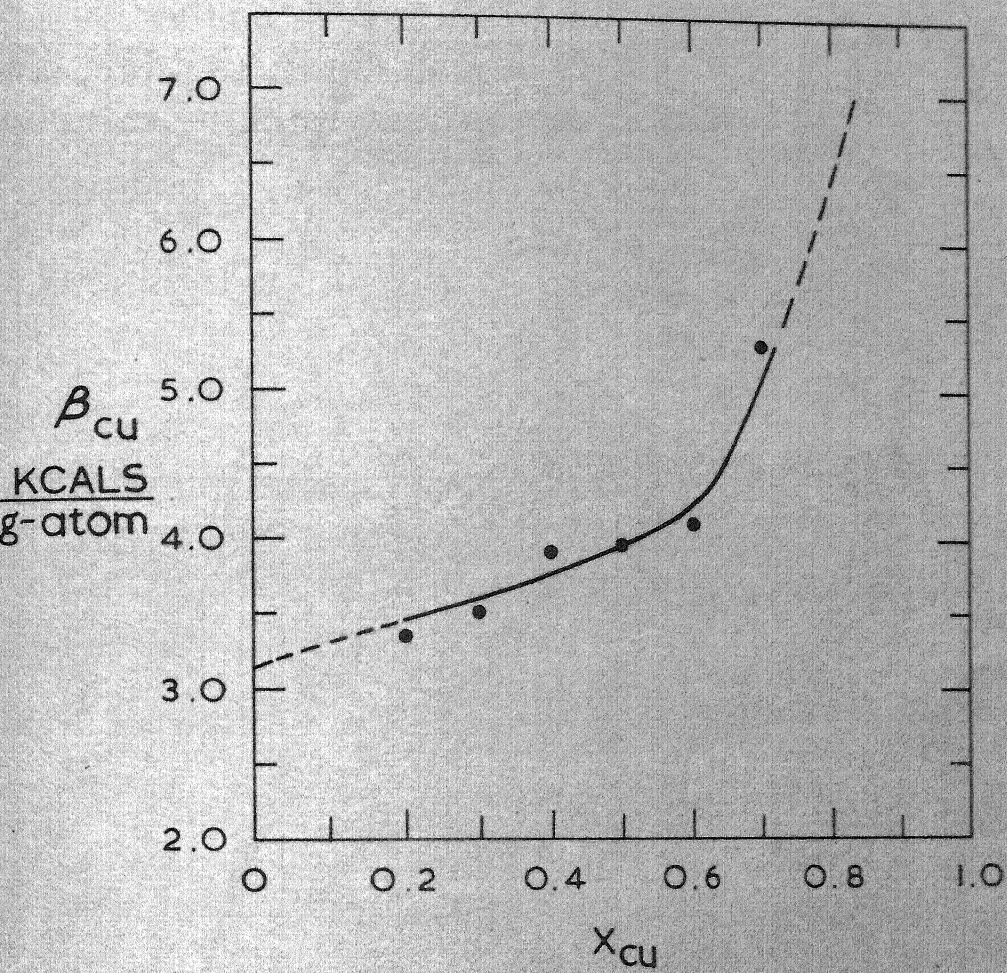
FIG. 5
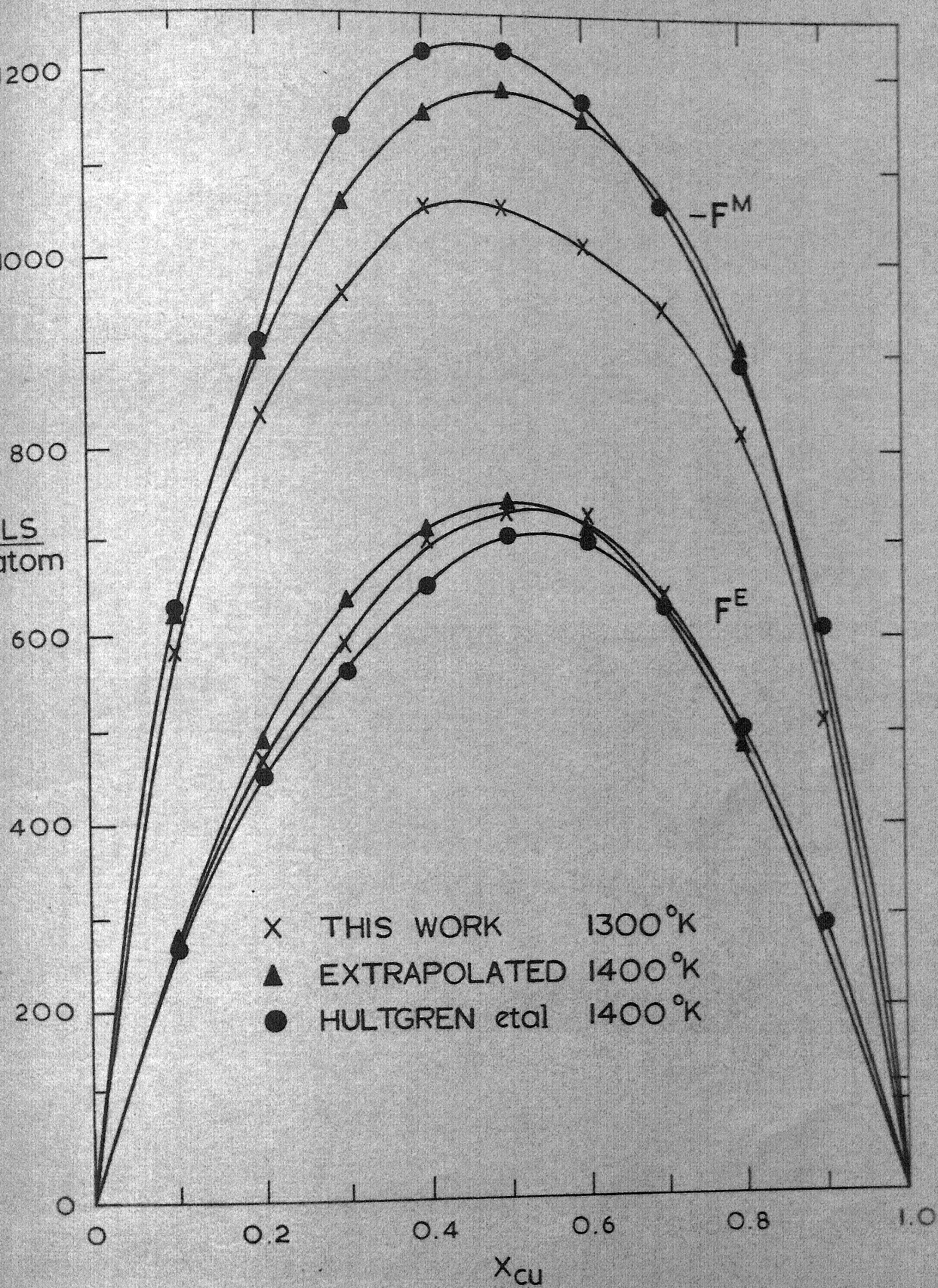
FIG. 6
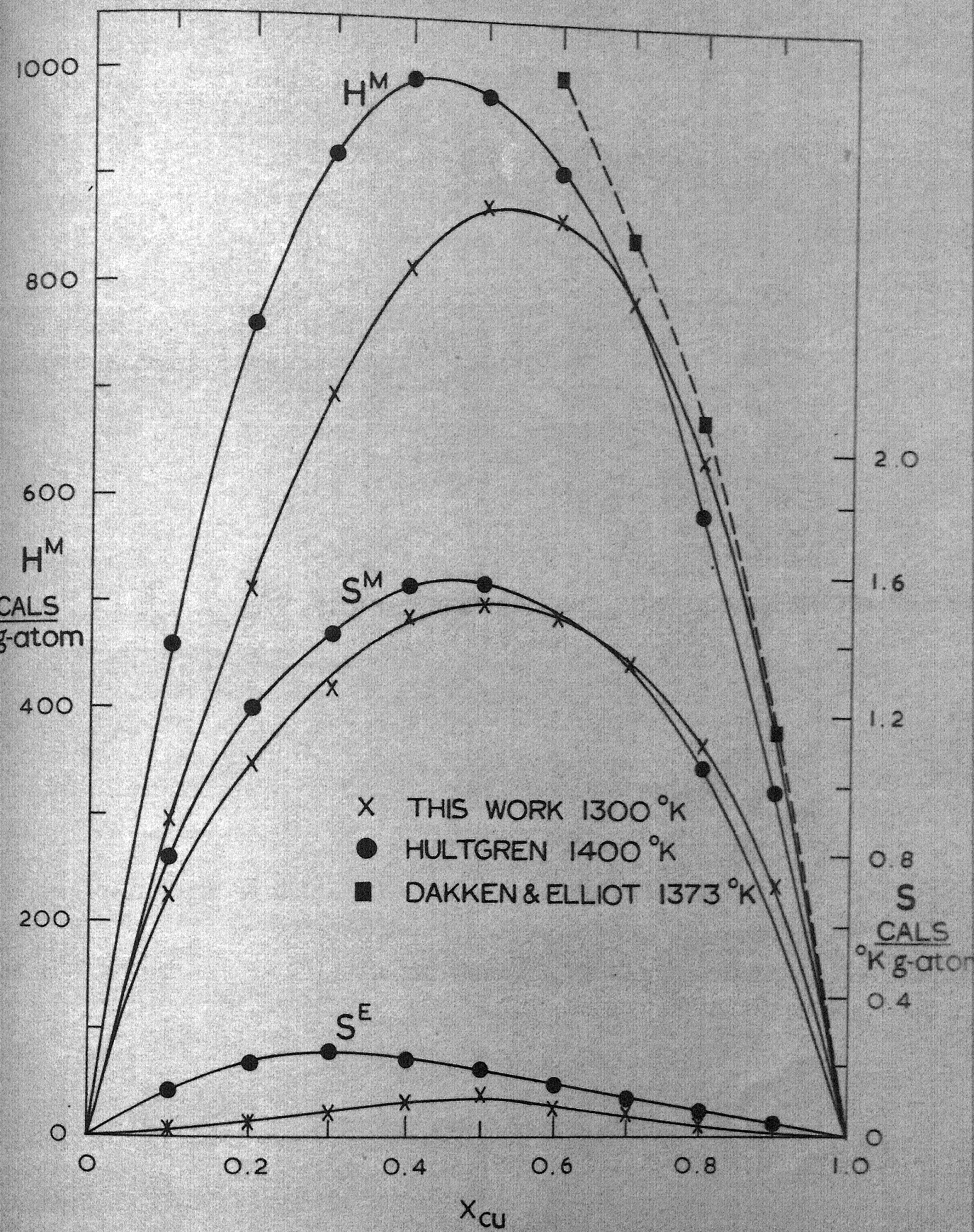
FIG. 7
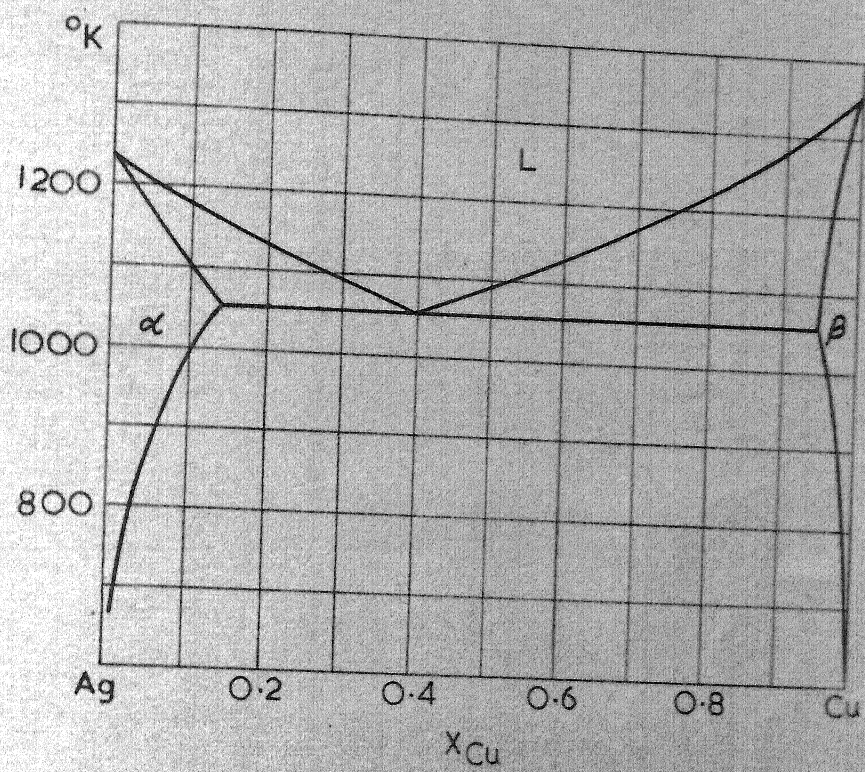
PHASE DIAGRAM OF COPPER-SILVER SYSTEM

FIG. 8

TABLE I.

Comparision of measured emf values for Calibration Cell Ni-NiO/C-C-ZrO2/Cu-Cu2O with the values reported in literature

Temperature (°K)	1173	1232	1273	1116	1150	1200	1323	1153	1020
Emf (mv)									
+This work	264.2	259.2	256.7	269.3	266.3	263.6	255.0	265.6	275.9
*Rizzo, Bidwell and Frank	265.6	261.4	259.5	269.6	267.2	263.7	—	267.0	276.5
*Charette and Flengas	264.0	259.9	257.0	268.1	265.7	262.1	253.5	265.4	275.8

+ Experimental values in the order of measurement - This work

* Calculated values from temperature - Emf relations of the authors

Rizzo, Bidwell and Frank (9.111) - E = 349.1 - 0.0712 T (973-1300°K)

Charette and Flengas (108) - E = 346.68-0.07046 T (924-1328°K)

TABLE II.

Experimental data on Liquid Cu-Ag alloys

X_{Cu}	Temperature range of applicability ($^{\circ}K$)	Emf (mV) $E = -\dfrac{C+DT}{D}$		Standard deviation (mV)	Maximum deviation (mV)
		$-C$	D		
0.1	1181–1330	191.1	0.2606	0.7	1.6
0.2	1133–1330	229.4	0.2470	0.6	1.0
0.25	1113–1330	245.6	0.2472	0.9	2.1
0.3	1090–1330	210.6	0.2132	0.4	1.0
0.4	1052–1330	196.6	0.1909	0.4	1.1
0.5	1090–1330	177.8	0.1657	0.6	1.2
0.6	1131–1330	163.8	0.1485	0.4	0.7
0.7	1173–1330	157.6	0.1370	0.5	0.9
0.8	1220–1330	140.4	0.1190	0.8	1.0

TABLE-III (3)

Activities in liquid Cu-Ag alloys at 1200°K and 1300°K

N_{Cu}	a_{Cu}^{+} (ε_s)(S)	a_{Cu}^{*} (ℓ)	γ_{Cu} (ℓ)	a_{Ag} (ε)	γ_{Ag}	a_{Cu} (ε)	γ_{Cu}	a_{Ag}	γ_{Ag}
	1200°K					1300°K (±2°)			
0.1	0.300	0.264	2.640	0.914	1.016	0.268	2.545	0.912	1.013
0.2	0.523	0.447	2.235	0.846	1.057	0.419	2.094	0.844	1.055
0.3	0.646	0.552	1.840	0.786	1.122	0.524	1.737	0.777	1.110
0.4	0.731	0.625	1.563	0.737	1.228	0.599	1.498	0.719	1.198
0.5	0.816	0.698	1.396	0.686	1.372	0.676	1.358	0.658	1.316
(±0.005)					(±0.007)	(±0.008)	(±0.018)	(±0.009)	(±0.019)
0.6	0.870	0.744	1.240	0.629	1.573	0.770	1.231	0.600	1.501
0.7	0.929	0.795	1.141	0.550	1.833	0.796	1.219	0.524	1.747
0.8	–	–	–	–	–	0.880	1.045	0.432	2.160

+ Standard state — Pure solid copper

* Standard state — Supercooled liquid copper

Table-III(b)

Activities in liquid Cu-Ag alloys at 1400°K

1400°K

X_{Cu}	$a_{Cu}^\dagger$	a_{Cu}^*	$\gamma_{Cu}^\dagger$	$a_{Ag}^\dagger$	a_{Ag}^*	$\gamma_{Ag}^\dagger$
0.1	0.246	0.221	2.460	0.910	0.918	1.011
0.2	0.395	0.348	1.975	0.840	0.852	1.050
0.3	0.501	0.468	1.668	0.773	0.770	1.104
0.4	0.578	0.600	1.444	0.715	0.678	1.151
0.5	0.660	0.675	1.321	0.646	0.615	1.232
0.6	0.720	0.738	1.198	0.585	0.552	1.262
0.7	0.775	0.791	1.110	0.509	0.485	1.662
0.8	0.835	0.846	1.043	0.402	0.384	2.610

† Extrapolated activity values from this work

* Values reported by Hultgren et al (8)

Table IV.

Thermodynamic functions of mixing at 1300°K in liquid copper–silver alloys

x_{Cu}	$-F^M_{Cu}$	H^M_{Cu}	S^M_{Cu}	α_{Cu}	β_{Cu}	$-F^M_{Ag}$	H^M_{Ag}	S^M_{Ag}	$-F^M$	H^M	S^M
0.1	3530	*2675 +(1290)	*4.77	0.500	*1310	250	95	0.21	580	295	0.67
0.2	2250	2170	3.40	0.502	3190	485	100	0.75	935	510	1.04
0.3	1670	1735	2.62	0.497	3500	660	255	0.70	695	695	1.25
0.4	1385	1415	2.15	0.505	3920	950	455	1.00	1065	815	1.46
0.5	1000	980	1.52	0.579	3950	1125	795	1.46	1065	1065	1.50
	(±30)	(±240)	(±0.18)	(±0.026)	(±490)	(±35)	(±260)	(±0.2)	(±25)	(±190)	(±0.14)
0.6	810	655	1.13	0.583	4100	1120	1130	1.90	1015	765	1.45
0.7	640	480	0.86	0.618	5320	1670	1560	2.50	950	780	1.34
0.8	465	120	0.45	0.490	*6400	2170	2100	3.30	985	660	1.11

* Extrapolated values from graph

+ Experimental values

APPEDIX-A

Calibration Run   Run.No.1

Time (hrs)	Temperature °C	Emf (mV)	Variation in emf (mV)
00-23	900	264.2	0.3
20-33	959	259.2	0.4
45-55	1000	256.7	0.2
59-71	943	263.3	0.3
73-84	877	266.3	0.3
86-94	927	263.6	0.2
96-101	1050	255.0	0.5
102-105	949	260.1	0.1
107-119	880	265.6	0.5
121-131	747	275.9	0.4
134-144	731	269.6	0.5
147-155	897	265.2	0.3
157-165	1050	255.8	0.2
169-171	850	269.1	0.3
174-179	700	272	0.6

Run 2

$X_{Cu} = 0.7$ Master alloy Cell 1 Inconel – Inconel

Time (hrs)	00-03	04-06	07-08	09-11	12-20	21-22	23-26	27-30	31-32	33-35
Temp. (°C)	1003	977	950	808	780	750	1050	1077	1126	1080
Emf (mV)	17.15	13.9	10.2	5.0	3.2	3.3	24.8	27.8	30.3	28.3

	36-37	38-46	47-50	51-53
	1048	1007	912	980
	24.7	18.7	6.1	3.9

Run 3

$X_{Cu} = 0.8$ Master alloy Cell 1 Inconel – Inconel

Time (hrs)	00-02	04-07	09-13	14-17	18-19	20-25	26-27	28-29	30-33
Temp. (°C)	1001	1030	1050	1077	995	1063	1098	1127	990
Emf (mV)	11.1	14.5	17.0	19.2	19.5	19.9	20.9	21.9	10.2

Run 4

$X_{Cu} = 0.25$	Master alloy		Cell a		Inconel — Platinum		Thermal Emf $E=.0313T-6.25$ (800-1000°C)	
Time (hrs.)	00-03	04-08	10-18	19-21	22-25	28-32	34-36	39-44
Temp.(°C)	900	927	1000	977	950	1052	1027	901
Emf (mV)	65.8	75.0	92.8	97.4	90.1	106.7	101.2	65.4
Corrected emf	44.0	52.3	67.8	63.1	56.7	73.1	75.3	43.6

Run 5

	Master alloy $X_{Cu} = 0.85$			Cell a		Cermet – Cermet $X_{Cu} = 0.70$		
Time (hrs)	00-04	05-06	07-10	00-03	04-06	08-09	10-11	10-18
Temp.(°C)	1041	1088	1050	1029	1097	1117	1097	1030
Emf (mV)	12.8	7.5	14.0	22.7	27.5	29.6	27.8	22.8

Run 6

$X_{Cu} = 0.4$ Master alloy   Cell a   Cermet – Cermet

Time (hrs)	00-02	03-11	12-14	15-16	17-27	29-33	34-39	41-52	53-56	57-59	61-63
Temp. (°C)	1001	1050	1090	1113	1020	952	952	797	821	903	977
Emf (mV)	95.3	55.5	59.0	64.3	40.3	35.4	14.6	3.5	7.5	26.3	41.5

Run 7

$X_{Cu} = 0.1$ Master alloy   Cell a   Cermet – Cermet

Time (hrs)	00-04	05-12	14-16	17-20	22-31	32-36
Temp. (°C)	1050	977	930	1051	939	922
Emf (mV)	152.5	134.0	122.6	153.2	125.3	121.1

Run 8

$X_{Cu} = 0.2$ — Master alloy / Cell a / Cermet – Cermet

Time (hrs)	Temp. (°C)	Emf (mV)
00-02	964	74.5
03-10	1000	85.5
11-13	1016	90.0
15-18	1052	87.5
19-21	1002	86.1
23-25	950	72.8
26-32	912	63.2
33-36	872	53.5
37-40	937	45.3
42-45	801	48.2
47-49	850	51.3
50-52	863	65.6
53-65	933	71.9
66-69	988	93.8
70-71	1035	97.0
72-73	1051	

$X_{Cu} = 0.3$ — Addition

Time (hrs)	Temp. (°C)	Emf (mV)
77-80	1054	71.8
81-83	998	60.4
84-87	997	40.4
88-98	925	23.7
90-114	915	21.9
115-118	793	16.5
119-130	964	32.0
132-135	955	50.9
136-138	1018	65.0
139-144	1036	69.0
145-1..	1049	71.4

74.

Run 8 (Contd.)

$x_{Cu} = 0.4$ Addition

Time (hrs)	150-152	153-160	162-165	167-69	171-192	194-96	197-190	191-194	195-198	200-202	204-205
Temp. (°C)	1048	1005	943	887	826	766	730	816	823	871	1047
Emf (mV)	55.5	47.7	35.2	24.6	13.8	7.4	5.0	11.8	31.4	40.6	55.2

$x_{Cu} = 0.5$ Master alloy

Run 9   Cell a   Cermet – Cermet

Time (hrs)	00-03	06-12	14-18	19-22	24-28	29-35
Temp. (°C)	1004	907	837	930	1039	963
Emf (mV)	35.1	20.5	8.0	23.9	40.5	29.9

Run 10

Cell a — Cermet — Cermet

$X_{Cu} = 0.6$ Master alloy

Time (hrs)	00–04	08–14	16–19	21–23	25–31
Temp. (°C)	1052	979	1013	948	1051
EmF (mV)	33.0	7.5	27.4	16.8	32.9

$X_{Cu} = 0.5$ Master alloy

Run 11

Cell b — Cu_2O — Cu_2O

Time (hrs)	00–06	08–11	12–20	22–24	26–29
Temp. (°C)	1039	931	839	985	1015
EmF (mV)	35.4	21.8	6.3	30.9	36.3

$X_{Cu} = 0.6$ Contd.   Addition

Cell b — Cermet — Cermet

Time (hrs)	34–38	39–42	44–46	48–51	53–64
Temp. (°C)	1035	950	1002	927	1053
EmF (mV)	29.9	19.2	25.6	14.6	33.0

Run 11 (Contd.)

$X_{Cu} = 0.7$ Addition   Cell b   Cermet – Cermet

Time (hrs)	69–71	72–75	77–82	84–87	89–93	94–95	96–101
Temp.(°C)	1028	999	1028	1036	975	1016	1040
Emf (mV)	22.2	18.5	8.0	22.6	14.3	19.5	23.5

Run 12

$X_{Cu} = 0.1$ Master alloy   Cell a   Cermet – Cermet

Time (hrs)	00–02	04–07	09–14	15–18	20–24	25–28	30–34	36–39	40–48	50–49
Temp.(°C)	1053	949	922	997	1021	972	1064	931	998	912
Emf (mV)	155.0	127.5	120.0	940	146.2	134.0	156.4	122.2	76.5	109

Run 13

$X_{Cu} = 0.5$ Master alloy   Cell b   Cermet – Cermet

Time (hrs)	00–04	05–07	08–14	16–20	21–28
Temp.(°C)	1027	1056	927	1000	1051
Emf (mV)	7.2	9.25	2.7	2.8	8.4

APPENDIX - B

APPENDIX - C

Preparation of Solid Electrolyte Crucibles:

The crucibles prepared in the laboratory were done by two methods. For both these, starting material is ZIRCOA - B powder containing completely stabilized lime-zirconia solid solution. In the first method, these powders were cold pressed into compacts, sintered at $1000^{o}C$ for about 6 hrs. and holes were drilled in these. In the second method, slip of suitable consistency was prepared by grinding the ZIRCOA-B powder (- 325 mesh) with water in a pebble mill for one full day. The slip was poured into the plaster of paris moulds and excess amount was drained off after considerable wall thickness of the settled slip was built. The mould was allowed to dry and by slightly tapping, green shapes of crucibles were taken out of the mould. These were initially dried at $150^{o}C$ and then slowly heated to $1200^{o}C$. This initial sintering was done for one full day.

The partially sintered crucibles obtained by these two methods were polished on the outer surface to make it as smooth as possible. These were transferred to gas fired ZIRCOA-B pot furnace for the final sintering. These were arranged on the hearth away from the burner. To avoid the sticking of crucibles to the bottom, zirconia chips were placed below these crucibles. The firing schedule of the furnace was as follows:

		A.M.				P.M.		
Time	8.30	10.30	12	12.30	1	2	2.30	8
Oxygen Pressures PSI	30	40	50	50	60	60	75	80
Acetylene Pressures PSI	4	4	5	5	5	4	4	5
Temperature	R.T.	1200	1425	1525	1700	1960	2000	2000

Cooling Schedule	8.20	8.30	8.45	9	9.15	9.30	10P.M.
	75	70	65	65	55	45	
	3.75	3	3¼	3¼	3¼	3¼	
	1950	1850	1750	1700	1600	1550	1375

The furnace was sealed at 10 P.M. and opened after 18 hrs.

Sintered crucibles with densities of 5.5 to 5.9 were obtained.

Note: For a temperature of $2000^{o}C$, 70 : 4 or 60 : 4 $(O_2 : C_2H_2)$ is

recommended. Temperature was measured by an optical pyrometer

and was controlled by adjusting the acetylene and oxygen rates.

A full oxygen cylinder (1900 PSI) lasts for 2¼ hrs at 80 PSI.

A full acetylene cylinder (260 PSI) lasts for 64 hrs at 5 PSI.

With 5 oxygen and 4 acetylene cylinders, temperature can be

maintained for maximum of 15 hrs.

APPENDIX - D

Estimation of oxygen solubilities in liquid
Cu-Ag alloys using Belton and Tankin's model

This model is useful to estimate standard free energies of solution of oxygen in binary alloys from those of the metals. The estimates will be accurate if the solvent metals do not deviate widely from ideal behaviour and the heats of solution of solute in the seperate solvent metals do not differ by more than few kilo-calories. Oxygen dissolved is thought to exist as some sort of molecular species. According to this model, solubilities of oxygen in Cu-Ag are estimated as follows:

(i)   Equilibrium partial pressure of oxygen ($p_{O_2}^{o}$) over pure Cu and Cu_2O at the desired temperature is calculated.

(ii)   Activity of copper (a_{Cu}) corresponding to the desired composition and temperature are noted from the experimental data.

(iii)   Equilibrium p_{O_2} over Ag-Cu(l) and Cu_2O is calculated from the relation

$$p_{O_2}^{\frac{1}{2}} = p_{O_2}^{o\frac{1}{2}} / a_{Cu}^{2}$$

(iv)   Then, standard free energy of solution of oxygen in copper-silver alloys F_O^M (Cu-Ag) is calculated from the relation derived by Belton and Tankins

$$F_O^M(Cu-Ag) = RT \left[N_{Cu} \ln N_{Cu} + N_{Ag} \ln N_{Ag} \right] - H^M + \left[N_{Cu} F_O^M(Cu) + N_{Ag} F_O^M(Ag) \right]$$

where H^M is the measured or calorimetric value.

(a) F_O^M (Cu) at any temperature can be calculated from Belton and Tankins' (22) value for $\frac{1}{2} O_2 = \underline{O}$ (Cu) 1 at %

$$F_O^M \text{ (Cu)} = -9930 - 4.75 \text{ T} \ (1150 - 1650^{\circ}C)$$

(b) F_O^M (Ag) is obtained from Diaz and Richardson's (143) equation for $\frac{1}{2}O_2 = \underline{O}$ (Cu) 1 at %

$$- F_O^M \text{ (Ag)} = -3380 - 5.07 \text{ T} \ (\qquad 1100^{\circ}C)$$

(v) $\frac{1}{2} O_2 = \underline{O}$ (Cu - Ag) 1 at %

$$F_O^M \text{ (Cu-Ag)} = -4.576 \text{ T log K}$$

K is found out from the above relation

(vi)   Also $K = a_{\underline{O}} / P_{O_2}^{\frac{1}{2}}$

For 1 at % standard state, and reference state as infinitely dilute solution.

$$a_{\underline{O}} = N_{\underline{O}} \times 100 = \% \underline{O} \text{ (atm %)}$$

$$K = \% \underline{O} / P_{O_2}^{\frac{1}{2}}$$

$\therefore$ log $\% \underline{O} = - F_O^M$ (Cu - Ag)$/4.576$ T $+ \frac{1}{2}$ log P_{O_2}

Solubilities at $1200^{\circ}K$ and $1300^{\circ}K$ were obtained by the above procedure.

X_{Cu}	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
$1200^{\circ}K$	0.75	0.50	0.44	0.54	0.6	0.7	0.76	-
At % O								
$1300^{\circ}K$	1.5	0.93	0.90	1.00	0.92	1.04	1.1	0.99

APPENDIX - E

Uncertainity Analysis:

A typical uncertainity estimate is made for $X_{Cu} = 0.5$ alloy. As per convention, the uncertainity limit is taken as twice the standard deviation.

Uncertainities in temperature (dT) measurement is due to changes in temperature, thermal gradients and error in thermal calibration. Taking all these into account, d T will not be greater than $\pm 2^{0}$C in the present work.

Standard deviation of Emf vs. Temp. plot for $X_{Cu} = 0.5$ is ± 0.6 mV.

Hence uncertainity in measured emf = $\cdots \pm 1.2$ mV uncertainities in compositions (d X_{Cu} or d X_{Ag}) are estimated to be not greater than $\pm .005$.

F_{Cu}^{M} reported in the tables is with respect to liquid copper as standard state. Since free energy of fusion is considered to be accurate (error < 1 %), change of standard state barely affects the uncertainities in F_{Cu}^{M}.

At 1300^{0}K

$$F_{Cu}^{M} = RT \ \ln \ a_{Cu} = -FE$$

$$d \ F_{Cu}^{M} = -F \cdot dE \simeq 23 \times 1.2 \simeq 30 \ cals$$

$$d \ F_{Cu}^{M} = RT \ \frac{d \ a_{Cu}}{a_{Cu}} + R \ dT \cdot \ln \ a_{Cu}$$

$$\therefore \ d \ a_{Cu} = \pm \ .008$$

Percentagewise a_{Cu} at $1300^{\circ}K$ for $X_{Cu} = 0.5$ is around 1 %.

$$\gamma_{Cu} = a_{Cu}/X_{Cu}$$

$$d \; \gamma_{Cu} = \left(\frac{d \; a_{Cu}}{X_{Cu}}\right)^2 + (a_{Cu} \cdot d \; X_{Cu}/X_{Cu}^2)^{\frac{1}{2}}$$

$$= \pm .018$$

$$F_{Cu}^E = RT \; \ln \; \gamma_{Cu} \qquad\qquad \therefore \; d \; F_{Cu}^E = \pm 35 \; cals$$

$$\alpha_{Cu} = \log \; \gamma_{Cu}/X_{Ag}^2 \qquad\qquad \therefore \; d \; \alpha_{Cu} = \pm .02$$

$$S_{Cu}^M = d \; F_{Cu}^M/dT$$

(i) $\qquad d \; S_{Cu}^M = d \; (d \; F_{Cu}^M/dT) = 0.15$

(ii) $\qquad$ Also $d \; S_{fusion} = \pm 0.1$

Hence total uncertainities $d \; S_{Cu}^M$ (total) $= (0.15)^2 + (0.1)^2 = \pm 0.18$

$$H_{Cu}^M = F_{Cu}^M + T \; S_{Cu}^M$$

uncertainity in heat of fusion need not be considered because it is taken care of in S_{Cu}^M term.

$$\therefore \; d \; H_{Cu}^M = (d \; F_{Cu}^M)^2 + (T \cdot d \; S_{Cu}^M)^2 = \pm 235 \; cals$$

$$\beta_{Cu} = H_{Cu}^M/X_{Ag}^2 \qquad\qquad d \; \beta_{Cu} = \pm 480 \; cals$$

Similarly uncertainities in F_{Ag}^M, H_{Ag}^M, S_{Ag}^M; a_{Ag}, γ_{Ag}; F^M, H^M, S^M and F^E, S^E were calculated. These are reported in Table IV.

BIBLIOGRAPHY

(Copper-Silver system; Thermodynamics of metallic
solutions - solution models - Phase diagram
correlations)

1. N. KAWAKAMI: Heats of formation of liquid alloys
SCI. REP. TOHOKU UNIV. JAPAN, 19, 52, 1930.

2. M. RENDALL et al: Free energy of some copper compounds
IND. ENGG. CHEM., 23, 388, 1931.

3. R. K. EDWARDS and J.H. DOWNING: Thermodynamics of liquid
solutions in Cu-Ag system,   J. PHY. CHEM., 60, 108,1956.

4. M. HANSEN: 'Constitution of Binary alloys' MCGRAW-HILL,
1958.

5. P.J.KOROS and J. CHIPMAN: Activity coefficient of iron in
liquid iron and Fe-Cu alloys at 1600°C J.METALS, 8,1102,
1956.

6. (a) R.A.ORIANI: Heat of formation solid and liquid
alloys at 1100°C by calorimitry. J. PHY. CHEM.,
62, 327, 199, 1958.

   (b) R.H.DOKKEN and J.F. ELLIOT: (Heats of formation of
liquid Cu-Ag alloys for X_{Cu} > 0.5 at 1100°C) TRANS.
AIME., 233, 1351, 1965.

7. A. KRUPKOWSKI: Thermodynamics of solid solutions of
metals.   MEM.SOC.REV.MET, 59, 34, 1962.

8. R. HULTGREN et al: Selected values of thermodynamic
properties of metals and alloys. JOHN WILEY PUB. 1963.

9. D.R. YOUNG: Thermodynamic study of oxygen in molten
copper alloys Ph.D. Thesis, UNIV. OF LONDON, 1965.

10. O. REDLICH and A.T.KISTE: Algebric representation of
thermodynamic properties and the classification of solutio
IND. ENGG. CHEM., 40, 345, 1948.

11. J. CHIPMAN: Activities in liquid metallic solutions,
DIS. FAR. SOC., 4, 23, 1948.

12. J. CHIPMAN and J.E. ELLIOT: The thermodynamics of liquid metallic solutions. 'Thermodynamics in Phy. Met.', ASM 1950.

13. C. WAGNER: 'Thermodynamics of alloys' ADDISON-WESLEY PUB., 1952.

14. 'The Physical Chemistry of metallic solutions and inter-metallic compounds' Vol. 1 and 2, NATIONAL PHY. LAB. SYMP. 9, 1958.

15. C.B. ALCOCK and F.E. RICHARDSON: Dilute solutions in molten metals and alloys - Parts 1 and 2, ACTA.MET, 6, 385, 1958; 8, 882, 1960.

16. H.A. WREIDT: Calculation of activities in binary systems having miscibility gap, TRANS. AIME., 221, 377, 1961.

17. W.H. ROTHERY with O.J. ROAF: (a) On the theory of solid solutions of Cu, Ag and Au PHIL. MAG., 6, 55, 1961.

     (b) with C.J. COOKE: Structures of Cu, Ag and Au alloys, J. LESS. COMMON METALS, 10, 57, 1966.

18. R.A. ORIANI and C.B. ALCOCK: The applicability of some simple models to metallurgical solutions, TRANS. AIME., 224, 1104, 1962.

19. _____ The structure of liquid metals and alloys MET. REV., 10, 385, 1965.

20. O. KUBASCHESKI and E.L.EVANS: Calculation of phase diagrams from thermochemical data   J. INST. METALS, 93(6), 329, 1965.

21. B. PREDEL: The constitution and thermodynamics of systems containing miscibility gaps, Z. MET. KUND., 56, 791, 1965.

22. G.R. BELTON and E.S.TANKINS: Thermodynamic behaviour of oxygen in liquid binary metallic solvents - a simple solution model, TRANS. AIME., 233, 1892, 1965.

23. P.V. RYSSELBERGHE: Some aspects of thermodynamic structure of electrochemistry,   MOD. ASPECTS. ELE. CHEM., P. 1-46, 1966 (4).

24. B.E. SUND QUIST: The calculation of thermodynamic Proper-ties of Miscibility gap systems, TRANS. AIME., 236, 1111, 1966.

25. S. NAGAKAURA et al: Lattice parameters and structures of Ag-Cu alloys rapidly quenched from liquid state, ACTA.MET., 14, 73, 1966.

26. L.S. DARKEN: Thermodynamics of binary and ternary metallic solutions, TRANS. AIME, 239, 80, 90, 1967.

27. R. HULTGREN: Problems and progress in thermodynamics of metals and alloys, J. METALS, 19(10), 31, 1967.

28. R. SPEISER: Some thermodynamical aspects of phase diagrams (in) 'Energetics in Metallurgical phenomena', Vol.1, W.M.MULLER, 1967.

29. O. KUBASCHEWSKI et al: 'Metallurgical Thermochemistry' 4th Ed., PERGAMON Press, 1967.

30. G.R. FITTERRER (Ed.): 'Application of fundamental thermodynamics to metallurgical processes', Proc., GORDON and BREACH Pub., 1967.

31. R.HISKES and W.A. TILLER: Generation of chemical potentials by analysis of phase diagrams - Part 1, 2 and 3, MAT. SCI. and ENGG., 2, 320, March 1968, 4, 163, 173, May 1969.

32. E.T. TURKDOGAN and L.S. DARKEN: Thermodynamics of metallic solutions - II, TRANS. AIME., 242, 1997, 1968; Part III - (To be published) Ab. J. METALS, 20, DEC. 1968.

33. P. BOLSAITIS and L. SKOLICK: Electron cell model of alloys, ibid 242, 215, 1968.

24. G.L.F. POWELL et al: The undercooling of Cu-O; Ag-O; Cu-Ag-O alloys, J. AUST. INST. METALS, 10, 23, 1965; TRANS. AIME., 239, 1244, 1967; ibid., 242, 2133, 1968.

35. I.T. SRYLIN et al: Application of various models to liquid metal alloys, R. J. PHY. CHEM., 42(3)376,1968.

36. A.G. MORACHESKI: Present state of studies on thermodynamic properties of binary and ternary liquid metallic systems, ibid p. 305.

37. H. THEO and B. PREDEL: Constitution and Thermodynamic properties of alloys, ARCH. EISEN, 39, 783, 1968.

38. C.H.P. LUPIS: On the polynomials for Thermodynamics of metallic solutions, ACTA. MET, 16, 365, 1968.

39. W.G. HENRY et al: The effect of electronic and structural parameters on the thermodynamic properties of liquid alloys (To be published) in PHY. CHEM of LIQUIDS.

40. J. R. GUDANGO: Molecular structure in liquid alloys-interpretation of structure from thermodynamic values (To be published) Ab. J. METALS, 20 JAN. 1968.

41. P.S. RUDMAN: (i) Synthesis of binary phase diagrams from thermodynamic data. (ii) Analysis of binary phase diagrams for thermodynamic data (To be published) Ab. J.METALS, 20, AUG. 1968.

(Solid electrolytes - Classified references according to various metallurgical applications)

A. REVIEWS AND GENERAL REFERENCES

42. K. KIUKKOLA and C. WAGNER: Galvanic cells for the determination of standard free energy of formation of metal halides, oxides, sulphides at elevated temperatures. J. EL. CHEM. SOC., 104, 308, 379, 1957.

43. 'Electrochemistry of molten and solid electrolytes'- Translation from Russian CONSULTANTS BUREAU 1961.

44. H. SCHMALZRIED: (a) ZrO_2 as electrolyte in electro-chemical investigations at elevated temperatures Z. ELE. CHEM., 66, 572, 1962.

(b) Ionic and electronic conductivity in binary oxides (MgO, Al_2O_3, ZrO_2-CaO, SiO_2, Rare earths, Al_2O_3 . SiO_2) Z. PHY. CHEM., 38, 87, 1965.

45. H. MOEBIUS: Oxygen ion conducting solid electrolytes Z. CHEM., 4, 81, 1964; Z. PHY. CHEM (L)., 230, 396,1965.

46. K. GOTO and Y. MATSUSHITA: (a) On the application of oxygen concentration cells with the S.E. Zirconia-Calcia, to the basic research works in process metallurgy, J. FAC. ENGG. UNIV. TOKYO (B), 26 (1), 217, 1964.

(b) The application of oxygen concentration cells with the ZrO_2-CaO S.E, to thermodynamic and Kinetic studies at high temperature J. EL. CHEM. SOC. JAPAN, 35(1), 1,1967.

47. B.C.H. STEELE and C.B. ALCOCK: (a) Factors influencing the performance of solid electrolytes in high temperature thermodynamic measurements TRANS. AIME., 233, 1359, 1965

(b) Solid electrolytes - 'Science of Ceramics' Ed. Stewart 2, 397, 1963.

48. R. LITTLE WOOD: A review of emf methods for oxygen determination in molten alloys CANADIAN MET. QUART., 5(1), 1966.

49. C. WAGNER: (Applications of solid electrolyte galvanic cells for thermodynamic measurements), ADV. in ELE. CHEM and ELE. CHEM. ENGG., 4 , INTERSCIENCE PUB., 1966.

50. N. BIRKS: Solid state galvanic cells and the metallurgist J. SHEFFIELD UNIV. MET. SOC., 6, 56, 1967.

51. D.O. RALEIGH: Solid state electrochemistry 'Progress in solid state chemistry' Vol. 3, P. 84-132, Ed-H.REISS, PERGAMON Press, 1967.

52. C.B. ALCOCK (Ed): 'Electromotive force measurements in high temperature systems', INST. MIN. and MET. Publication, LONDON, 1968.

53. H. RICKERT: Thermodynamic and Kinetic studies of solid/gas systems especially by electrochemical methods, WERK. STOFFE. U. CORROSION, 19(10), 869, 1968.

54. H. SCHMALZRIED: Electrochemical methods (Zirconia-Calcia) to determine diffusion coefficients and phase limit reaction constants in and at solids, ARCH. EISEN., 39, 531, 1968.

55. H.S. SPACIL and D.L. SCHROEDER: The importance of oxygen partial pressure measurements in the metals industry using solid electrolytes, (To be published) Ab. J. METALS 19 Sept. 1967.

B. PHYSICAL PROPERTIES

56. F. HUND: The fluorite phase, its defects structure and electrical conductivity in the systems ZrO_2-CaO, ThO_2-Y_2O_3 and others, Z. PHY. CHEM., 199 , 142; 1952; 201, 268; 1952, BER. DEUTSH. KERAM. GES., 42 251, 1965.

57.　A. HOFFMANN and W.A. FISHER: The fluorite phase in the ternary systems $CaO-ZrO_2-Fe_2O_3$ and $CaO-ZrO_2-FeO_{1.07}$, Z.PHY.CHEM., 17, 30, 1958.

58.　W.D. KINGERY etal: Oxygen ion mobility in cubic $Zr_{0.85}Ca_{0.15}O_{1.85}$ J. AM.CER. SOC., 42, 393, 1959.

59.　S.P. MITTOF: Electrical conductivity in single crystals of MgO J. CHEM. PHY., 31, 1261, 1959; 33, 940, 1960; 36, 1383, 1962.

60.　W.D. KINGERY and J.PAPPIS: Electrical properties of single and polycrystalline Al_2O_3 at high temperatures, J. AM.CER.SOC., 44, 459, 1961.

61.　S.F. PAL'GUEV and A.D. NEUIN: Electrical Conductivities of Be, Mg, Se, Ca oxides at high temperatures SOV. PHY. SOLID. STATE, 4, 629, 1962.

62.　M. HOCH: Formation of cubic ZrO_2 with transition metals of groups V and VI and their oxides J. AM. CER. SOC., 45, 373, 1962.

63.　T.Y. TEIN and E.C. SUBBA RAO: X-Ray and electrical conductivity of fluorite phase in $CaO-ZrO_2$ system, J. CHE. PHY., 39, 1041, 1963.

64.　W.A. FISHER: The electrical conductivity of $CaO-ZrO_2$ fluorite phase with Fe_2O_3 and $FeO_{1.01}$ between 800 and 1700°C Z.PHY. CHE., 35, 95, 1962.

65.　J. DIXON et al: Electrical resistivity of stabilized ZrO_2 at elevated temperatures J. ELE. CHEM. SOC., 110, 276, 1963.

66.　D.T.BRAY and U. MESTEN: Transport numbers in stabilized ZrO_2 ibid., 111, 100, 1964.

67.　D.M.ROY and R.ROY: Controlled massively defect crystalline solutions with fluorite structures ibid., P. 421.

68.　S.TYRIN: Grain boundary conductivity in CaO stabilized ZrO_2 J. APP. PHY., 35, 122, 1964.

69.　D.W. STEICKERS and W.G. CARLSON: Ionic conductivity of cubic solid solutions in the system $CaO-Y_2O_3-ZrO_2$.

70.　E.C. SUBBA RAO and H. SUTTER: Order disorder and ionic conductivity in stabilized ZrO_2, J. PHY. CHEM. SOLIDS, 25, 148, 1964.

71. T.MATSMURA: (Conduction in Al_2O_3)
     CAN. J. PHY., 44, 1685, 1966.

72. H.H. MOEBIUS: Electrical conductivity in the systems
     ZrO_2-CaO, ZrO_2-MgO SILICA TECHNIKA?, 17, 358, 1966
     Ch. Ab. P58505, 66, 1967.

73. C.F. CLINE et al:.   (Ionic conduction in BeO) J.AM.CER.
     SOC., 50, 55, 1967.

74. R.A. RAPP et al: Mixed conduction in (a) ThO_2 and ThO_2-
     Y_2O_3 solutions (b) ZrO_2-CaO and ThO_2-Y_2O_3 (c) Solid oxide
     electrolytes Z. PHY. CHEM., 49, 198, 1966; J.EL. CHEM. SOC.
     114, 752, 1967; 'Thermodynamics of Nuclear materials',
     1967, I.A.E.A., VIENNA, 1968.

75. L.E.SIMPSON and R.E. CARTER: Oxygen exchange and diffusion
     in CaO stabilized ZrO_2 J. AM. CER. SOC., 49, 139, 1966.

76. H. ULMANN: Limit of working temperature of O_2 measuring
     electrolyte cells with ThO_2 and ZrO_2 as S.E. Z. CHEM., 7(2)
     65, 1967.

77. R.J. RUKA etal: Seebeck coefficient of a $(ZrO_2)_{0.85}$
     $(CaO)_{0.15}$ electrolyte thermocell J.EL.CHEM.SOC., 115, 257, 1968.

78. C.B.ALCOCK: Transport of ions and electrons in ceramic
     oxides   Refer 52, P. 109.

79. R.E. CARTER and W.L. ROTH: Conductivity and structure
     in Calcia stabilized ZrO_2 Refer 52, P. 125.

Also, Refer 42; 43, P.63-104;44-47;52,P3

C. THERMODYNAMICS OF BINARY AND COMPOUND OXIDES AND
    NONSTOCHIOMETRY

80. S.ARONSON etal: Study of nonstoichiometry in UO_2 and
     UO_2 - ThO_2 solid solution using ZrO_2-CaO S.E.   J.CHE.
     PHY., 29, 151, 1958; 32, 749, 1960, 35, 1055, 1961.

81. . ... ..:

81.   H. SCHMALZRIED: The measurement of reaction free energies
      for the spinelphases AB_2O_4 ($AO+B_2O_3 = AB_2O_4$) using galvanic
      cells Z. PHY. CHEM(F), $\underline{25}$, 178, 1960.

82.   Y. GERASINV etal: Standard free energy of WO_2 DOKAL.
      AKAD. NAUK. USSR. $\underline{34}$, 1350, 1960.

83.   T.N. REZUKHINA et al: Determination of thermodyhamic
      functions of $CaWO_4$ by emf method R.J.PHY.CHEM.,$\underline{35}$, 671,1961.

84.   R.N. BLUMENTHOL et al: Electrochemical measurements of
      elevated temperature thermodynamic properties of certain
      Fe and Mn oxide mixtures   J. AM. CER. SOC., $\underline{44}$, 508, 1961.

85.   M. HOCH et al: Interaction energies of vacancies in
      transition metal oxides (NbO, NbO_2) with large concentration
      of vacancies   J. PHY. CHEM. SOLIDS, $\underline{23}$, 1463, 1962.

86.   H. J. ENGELL: The equilibrium measurements of mixed
      oxides   Z. PHY. CHEM (F), $\underline{35}$, 192, 1962.

87.   T.D. TRETCJAKOV: (Compound oxides) Z. ANORG. CHEM. USSR
      '$\underline{8}$, 145, 1814, 1963.

88.   R.A. RAPP: The free energy of formation of MoO_2 TRANS!
      AIME, $\underline{227}$, 371, 1963.

89.   T.N. REZUKHINA et al: Thermodynamic properties of aluminates
      using solid electrolytes (a) R.J. PHY. CHEM., $\underline{37}$, 358,
      1963 (b) $CaTiO_3$ ibid., $\underline{38}$, 1587, 1964. (c) (Double Oxides)
      ELECTROKHIMIYA., 1, 237, 467, 1965.

90.   R.BLUMENTHALL etal: (a) Thermodynamic study of phase equi-
      libria in Ti-O system J. ELE. CHEM. SOC., $\underline{110}$, 92, 1963.
      (b) Nonstoichiometric Nb_2O_5 (ZrO_2-CaO) J. AM.CER.SOC.,$\underline{48}$,
      617, 1965.

91.   K. KIUKKOLA: High temperature electrochemical study of
      Uranium oxides in the UO_2-U_3O_8 region, ACTA, CHEM,SCAND.,
      $\underline{16}$, 327, 1962.

92.   G.B. BARBI: Thermodynamic functions and phase stability
      limits by emf measurements with CaO-ZrO_2 S.E. (NiO, Fe_3O_4,
      WO_2 and MoO_2) J. PHY. CHEM., $\underline{68}$, 1025, 1964.

93.   H. SCHMALZRIED and R.W. TAYLOR: Thermodynamics of spinel
      phases (chromites, ferrites and aluminates) BER. BUN. PHY,
      CHEM., $\underline{69}$, 396, 1965.

., Bonder and ., ... :

94. G.A.ROEDER and W.W.SMELTZER: Dissociation pressures of iron-nickel oxides using ZrO_2-CaO S.E   J.EL.CHEM. SOC., 111, 1074, 1964.

95. W.L.WORRELL: Measurements of the thermodynamic stabilities of the Nb and Ta oxides using a high temperature galvanic cell 'THERMODYNAMICS VOL. 1' IAFA SYMP. 1965 P.131.

96. T.L. MARKIN etal: Measurement of oxygen potential of substoichiometric (i) PuO_2 ibid, P. 145, (ii) mixed U, Pu oxides – Paper presented at 3rd INT. CONF. on PLUOTINIUM, (LONDON, NOV. 1965).

97. A.G. BRERGERS: Hypothesis on high temperature solid state galvanic cell composed of refractory metal electrodes and ZrO_2-CaO S.E.,   J. AM. CER. SOC., 48. 123, 1965.

98. L.M.LENEV: Thermodynamics of Co and Ni Chromite, R.J.PHY. CHEM., 40, 1097, 1966.

99. L.R. BIDWELL etal: (a) Thermodynamics of W-O system TRANS. AIME, 239, 1901, 1967.
(b) Std. free energy of formation of cuprous oxide ibid, p. 539.
(c) Std. free energy of formation of cupric oxide, J.EL. CHEM. SOC., 114, 30, 1967.

100. C.B.ALCOCK and S.ZADOR: Thermodynamic study of Mn-MnO system using ThO_2-Y_2O_3 S.E,   ELE.CHIM. ACTA, 12, 673,1967.

101. S.ZADOR: Nonstoichiometric measurements in dioxides of rutile structures Refer 52, P. 145.

102. B.C.H. STEELE: High temperature thermodynamic measurements involving solid electrolyte systems Refer 52, P.3.

103. V.J.WHEELER etal: Galvanic cells and gas equilibration techniques,   PRO. BRIT. CER. SOC., 8, 51, 1967.

104. C.B.ALCOCK and S.ZADOR: (Nonstoichemetric studies using S.E.) ibid, 8 231, 1967.

105. T.N. REZUKHINA etal: Thermodynamics of higher Ti oxides (ThO_2-La_2O_3 S.E) IZV. AK.NAUK.USSR, NE.RG.MATER,3(11),101,196

106. H.SCHMALZRIED etal: Coulometric titration for studies of point defects in metal oxides (ZrO_2-CaO). BER.BUN.PHY.CHEM., 72, 745, 1968.

107. S. IGNATOWICZ etal: Free energy of formation of NbO and Ta_2O_5 using ThO_2-Y_2O_3 and ThO_2-CaO   J.LESS. COMMON METALS, 15(1), 100, 1968.

108. G.G.CHARETTE and S.N. FLENGAS: Thermodynamic properties of oxides of Fe, Ni, Pb, Cu and Mn by emf measurements J.EL.CHEM.SOC., 115, 796, 1968.

109. V.B. TARE and W.L. WORRELL: High temperature thermo-dynamic stability of oxide phases in V-O system (To be published) Ab. J. METALS, 20, JAN. 1968.

Also, Refer, 42; 44a; 45; 46a, 47; 51

D. ACTIVITY DETERMINATIONS IN LIQUID AND SOLID SOLUTIONS OF METALS AND OXIDES

110. R.E. CARTER: Dissociation pressures of solid solutions from Fe_2O_4 to 0.4 Fe_3O_4-0.6 Co Fe_2O_4(ZrO_2-CaO) J.AM.CER. SOC., 43, 448, 1960.

111. R.BENZ and H. SCHMALZRIED: Activity measurements in liquid PbO - SiO_2 solutions Z. PHY. CHEM(F), 29 77, 1961.

112. R.A. RAPP and F. MAAK: Thermodynamic properties of Cu-Ni alloys by S.E. (ZrO_2-CaO) method ACTA.MET.,10, 63, 1962.

113. T.N. REZUKHINA etal: Thermodynamic investigations of alloys by emf methods using ThO_2-La_2O_3 S.E
    (a) Co_3W R.J.PHY.CHEM., 36, 637, 1962.
    (b) Co-Mo and Co-Nb alloys ibid., 39, 70, 75, 1965.

114. M. SUNDARESAN etal: Thermodynamic properties of Fe-Pd alloys (ZrO - CaO)   ibid, 37, 1330, 1963.

115. I.V. GORDEEV etal: (a) Thermodynamics of solid solutions of (Fe B)$_3O_4$ where B = Mg, Mn, Ni using S.E.   R.J.INORG. CHEM., 8, 943, 1963; 9, 89, 1964.
    (b) Activity of FeO in (FeO-MgO) solid solutions at 900-1200°C using ZrO_2-CaO   VESTEN.MOSKOW UNIV.SER.II.KHIM., 18, 32, 1963.

116. C.R.CAVANAUGH and J.F.ELLIOT: The activity of Ni in liquid Pb-Ni alloys (ZrO_2-CaO) TRANS.AIME., 230, 633, 1964.

117. A.U.SEYBOLT: Activity of Ga in Ni Ga and associated Ga-Ga oxide equilibria by S.E. ZrO_2-CaO J. EL. CHEM. SOC., 111, 697, 1964.

118. K. SCHWERDTFEGER and A. MUAN: Activity measurements in Pt-Ni; Pd.-Ni and Pd-Co alloys using ZrO_2-CaO S.E. ACTA. MET., 13, 509, 1965.

119. L.R.BIDWELL etal: (a) The relative thermodynamic properties of Ni-Pd alloys using ZrO_2-CaO S.E ibid., p.61

(b) The activity of Cu in solid Cu-Pt alloys and some observations on the ordering of Cu_3Pt ibid, 15, 1143,1967.

120. C.M.SELLARS and F.MARK: Thermodynamic properties of Au-Ni alloys between 775 and 935°C TRANS. AIME., 236 457, 1966.

121. A. KUBIK and C.B. ALCOCK: (a) Thermodynamic study of solid Fe-Au and Co-Au alloys by the use of S.E., METAL, SCI. ᵀ., 1, 19, 1967.

(b) Activities in solid binary alloy systems Refer 52,p.43.

(c) The thermodynamic properties of phase solid solutions formed between Pd, Pt and Fe using ThO_2-Y_2O_3 and ZrO_2-CaO

as S.E. ACTA.MET., 17, 437, April 1969.

122. S. SEETHARAMAN and K.P. ABRAHAM: Activity measurements in double oxide slags using ThO_2-Y_2O_3 S.E

(i) NiO-MnO TRANS. IMM., 77, C210, DEC. 1968.

(ii) NiO-MgO . IND.J.TECH., 6, 123, 1968.

123. R.J.FREUHAN: Activity of Cr in liquid Ni-Cr alloys at 1600°C (ZrO_2-CaO) TRANS.AIME, 242, 2007, 1968.

124. S.C. SINGHAL and W.L. WORREL: High temperature thermodynamic properties of refractory metal alloys (ThO_2-Y_2O_3) (To be published)

(i) Ta-Mo system Ab. J.METALS 20, AUG.1968.

(ii) Ta-W system Ab. ibid, DEC. 1968.

125. G.R.FITTERRER etal: The determination of the phase boundaries in the system (i) Cr-Ni (ii) Co-Pt (To be published) Ab., J. METALS 21, March 1969.

126. Activity measurements in Pb-Sn system (ZrO_2-CaO) Refer 46a.

E. OXYGEN POTENTIALS IN METAL MELTS AND GAS MIXTURES

127. (a) H.PETERS and H.MOEBIUS: Electrochemical investigations of the equilibrium $CO + 1/2 \ O_2 = CO_2$; $C + Co_2 = 2 \ CO$ Z. PHY. CHEM., 209, 298, 1958.

   (b) H.PETERS and G.MANN: ....$Fe + CO_2 = FeO + CO$ Z.ELE.CHEM., 63, 244, 1959.

128. J. WEISSBART and R.   . RUKA: Oxygen gauge   REV.SCI. INSTR., 32, 593, 1961.

129. V.P. LUZZINS: Determination of the effectiveness of elements as deoxidizing agents by emf methods   IZVEST. VVZ. CHEM. MET (R)., 9, 50, 1963.

130. M. OHTANI etal: (a) Oxygen content in liquid iron using MgO as electrolyte   TET. HAGANE (J),   49, 22, 1963. (b) Determination of Po_2 in Fe-C-O solutions (S.E) TRANS. IRON and STEEL INST. JAPAN , 6, 76, 1966.

131. R. LITTLEWOOD: (Measurement of po_2 in gas mixtures) STEEL TIMES, P 423, 1964.

132. A.MITCHELL: (Measurement of po_2 in gas mixtures) NATURE, 201 (4917); 390, 1964.

133. K.GOTO and Y. MATSUSHITA: (a) Quick analysis of oxygen in iron melts TET.HAGANE (J), 50, 1821, 1964; 51, 443, 1965, 'Thermodynamics' Vol. 1 P 111, I.A.E. A VIENNA 1966 (b) po_2 measurements in waste gas of open hearth   ibid, 52, 393, 1966. (c) Measurement of po_2 in liquid Fe (ZrO_2-CaO) TRANS. IRON and STEEL INST.JAPAN, 6, 131, 1966.

134. T.N. BEDFORD and C.B. ALCOCK: Thermodynamics and solubility of oxygen in liquid metals (Pb and Sn) from emf measurements involving S.E's.   TRANS. FAR. SOC., 60, 822, 1964; 61, 443, 1965.

135. Electrochemical determination of oxygen activity in molten metals using ZrO_2-CaO S.E. (Geselschaft zur foerdung dur eisenhutten-technish m.v.h) NETH.APPL., 6, 604, 278 (C1, gG 0/n) OCT 10, 1966 GER.APPL., APRIL 8, 1965.

145. K. SCHWERDTFEGER: Measurement of oxygen activity in Fe, Fe-Si; Mn and Fe-Mn melts using ZrO_2-CaO ... TRANS. AIME., 239, 1277, 1967.

146. N.A.D. PARLEE etal: (a) Application of solid electrolyte Cell (ZrO_2-CaO) for measuring equilibrium p_{O_2} over liquid metal-oxygen solutions ibid, p. 1994.
(b) Oxygen-oxide equilibria in Ag-Cu alloys ibid, P.2005

147. J. OSTERWALD etal: Coulometric determination of the miscibility gap between liquid copper and Cu_2O, Z. METALKUNDE., 59, 576, July 1968.

148. J.K. PARGETER: A method for direct oxygen determination in molten metals (steel), J. METALS, 20, 74, June 1968.

149. W.A. FISHER and J. DIETER: Electrochemical determination of the oxygen partial pressures in steam-hydrogen mixtures and iron melts containing oxygen (1550-1750°C) ARCH.EISEN., 39, 89, 1968.

150. K. BOROWSKII etal: Continuous measurement of oxygen activity and carbon content in oxygen converter using S.E's ZrO_2-CaO; ThO_2-Y_2O_3 ibid, P. 259.

151. R. J. FREUHAN and E.T. TURKDOGAN: (a) Development of galvanic cell for the determination of oxygen in liquid steel (To be published) Ab., J. METALS, 20, DEC. 1968.
(b) Activity of oxygen in liquid Fe-Cr-O system ibid.

Also,   Refer   46;   48;   55

F: KINETIC APPLICATIONS

152. K. GOTO etal: (a) Rates of reduction and oxidation of oxides (FeO, Fe_2O_3, Fe_3O_4) by S.E. methods, TET. HAGANE(J), 50, 1818, 1964.

(b) Measurement of the rate of deoxidation of liquid steels by emf study of oxygen concentration cell ibid, 51, 1825, 1965.

(c) Measurement of p_{O_2} changes in oxide powders by oxygen concentration cells TRANS.AIME, 242, 82, 1757, 1968.

153.   H.RICKERT: Kinetic measurements with solid electrolytes
       Refer 52, P. 59.

154.   D.H. WAKELIN: The interaction between gas jets and the
       surfaces of liquids including molten metals (ZrO_2-CaO)
       Ph.D. Thesis, UNIV. OF LONDON 1966.

155.   C. GATELLIER etal: Use of emf measurements for kinetic
       study of deoxidation of liquid iron. COMPT. REND! (Fr),
       266 (26), 1753, 1968.

Also,   Refer   46a,   51,   53,   54

G.   DETERMATION OF DIFFUSION COEFFICIENTS

156.   H. RICKERT and R. STEINER: Diffusion of oxygen in silver
       by S.E. Method. Z. PHY. CHEM (F), 49, 1127, 1966.

157.   R.O. DOUGLAS: A rapid S.E. method for studying high
       temperature diffusion in metals J. EL. CHEM. SOC., 114,
       493, 1967.

158.   H. RICKERT etal: (a) Refer 52, p. 59
       (b) Electrochemical investigation of oxygen diffusion
       in liquid copper and silver (ZrO_2-CaO). Z. MET. KUND., 59
       (7), 635, 1968.

159.   J.C.BAZAN: A stationary electrochemical method of measuring
       diffusion coefficient of oxygen in metals (Ag) using
       ZrO_2-CaO as S.E.   ELE. CHIM. ACTA., 13(8), 1883, 1968.

460.   R.A. RAPPL: Diffusion and solubility of oxygen in
       solid copper   Refer 74 (iii)

161.   J.L. ISKOE and W.L. WORRELL: Polarization behaviour in
       high temperature galvanic cells designed to measure the
       diffusivity of oxygen in solids (To be published) Ab.
       J. METALS, 20, DEC. 1968.

162.   G.R. BELTON and F.H.HARVEY: The diffusivity of oxygen in
       liquid lead by steady state electrolyte cell technique,
       ibid.

163.   F.G.ARCEKLE and G.R. FITTERRER: Determination of diffusion
       coefficient of oxygen in liquid metals (Pb) by S.E.method,
       ibid.

H. MISCELLANEOUS APPLICATIONS

(i) ANALYSIS

164. T.C.WILDER and W.E. GALIN: Electrochemical determination of zinc content in molten grass using ZrO_2-CaO as S.E. (To be published) Ab., J. METALS, 20, DEC. 1968.

(ii) THERMOMETRY

165. W.T.LINDSAY and R.J.RUKA: Electrochemical thermometry a new approach to the determination of elevated temperature on thermodynamic scale ELE. CHIM. ACTA., 13, 1867, 1968.

(iii) CORROSION

166. E.J.MCIVER and S.TEALE: (Corosion studies of steels by galvanic cells) U.K.A.E.A. Ref. AERE - R 4942.

(iv) FUEL CELLS

167. J.WEISSBART and R. RUKA: A.S.E fuel cell J.EL. CHEM. SOC., 109, 723, 1962.